The PERFORMANCE of LUBRICATING OILS

by

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas.

Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline, second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

PREFACE

Lubricating oils are frequently called upon to perform under conditions which were unheard of a few years ago and under which the oils available at that time would have fallen far short. Mechanical improvements have resulted in more severe operating conditions, such as higher speeds, greater bearing loads, and higher temperatures, and it has been necessary to develop new and improved lubricants to keep pace with the mechanical advances. A good example is the hypoid gear, which is in common use in automotive equipment. This gear has certain mechanical advantages which make its use highly desirable, but it could not be put to practical use until special gear oils (EP lubricants) had been developed which were capable of preventing seizure under the conditions prevailing at the surfaces of the gear teeth. These conditions consist of high pressures and high rubbing velocities, which in turn result in high local temperatures. This example is by no means unique. Lubricants may be required to have fluidity at extremely low temperatures, antirust characteristics, the ability to peptize sludge particles, or any one of a number of highly specialized functions in addition to the basic one of reducing friction.

Much work has been done and many papers written on the performance of lubricating oils in various applications and under various conditions. The purpose of this Monograph is to assemble the salient features of this information under a single cover Two approaches were considered: one, a discussion of various oils according to application, e g., aircraft oils, gear oils, motor oils, turbine oils, various industrial lubricants, etc; the other, a discussion of the various performance characteristics, e g , oxidation, bearing corrosion, wear, etc. The first would enable the reader who is interested in a given single application to find all the information on that application in one chapter. However, such a treatise would require frequent revision to avoid becoming obsolete in a relatively short time It was largely for that reason that this approach was abandoned in favor of the second. The various performance characteristics are of a more basic nature than are the properties of a lubricant for a specific application, and it is hoped that a more permanent function

will be served with the present arrangement. Most of the discussion is based on work on lubricants for automotive equipment. This is because much more work has been done in this field and hence more knowledge is available. However, the conclusions should apply in related lubrication problems.

No attempt has been made to discuss refining methods in any detail, since books are available on this phase of lubricating oil technology, e.g., Kalichevsky's "Modern Methods of Refining Lubricating Oils". The sole purpose of the chapter on manufacturing methods is to acquaint the reader with the effect of each process step upon the performance characteristics of the resulting product.

The writer wishes to thank the Shell Oil Company for permission to publish this Monograph and to acknowledge his gratitude to his many colleagues both at Wood River and other parts of the Shell organization for their valuable assistance in its preparation.

Wood River, Illinois H. H. Zuidema
June, 1951

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Chapter I

PROCESS OF LUBRICATION

Introduction

Lubricants include substances having a wide range of physical properties. They are usually in the liquid state, although solids (graphite) and gases (air) may be used in certain applications. Liquid lubricants in turn vary widely in their physical properties. Mineral oils, ranging from extremely fluid liquids to highly viscous products, are commonly used. They may serve many purposes, such as conducting the heat of friction away from the bearings, serving as a seal to exclude undesirable substances from the area being lubricated, and acting as a carrier for rust preventives, antifriction agents, extreme pressure additives, and the like. However, their primary purpose is, in general, to lubricate, i e , to reduce friction. Many investigators have studied the mechanism of lubrication. As a result of their efforts certain phases of the subject are quite clearly understood. Others are still at the stage in which further research is required.

The type of lubrication depends largely upon the thickness of the lubricating film. Two fundamental types are discussed in this chapter—hydrodynamic (thick film) and boundary (thin film). The latter is subdivided further, and one type, extreme pressure or EP lubrication, is treated in some detail. While the different types of lubrication are clearly distinct, there is no sharp line of demarcation, but rather a gradual transition, between them This is true in the transition between hydrodynamic and boundary lubrication and also in the change from one type of boundary lubrication to another.

Hydrodynamic, or Fluid, Lubrication

When moving parts are separated by a film of oil thicker than about 6,000 Ångstrom units, or 1/40,000 of an inch, the laws of hydrodynamics apply in the film, and viscosity is the all-important factor as far as the oil is concerned There is no abrasive wear under ideal hydrodynamic conditions of lubrication since the moving parts never touch each other. The theory of hydrodynamic, or fluid, lubri-

cation is based upon the experimental work of Tower, dating back to 1885, and the theoretical work of Reynolds which followed shortly.[48, 29] Petroff, who was working independently at about the same time, arrived at similar conclusions regarding fluid lubrication.[48, 29] Petroff's work differed in that it is based on an oil film of uniform thickness, while Reynolds considered the more general case of films of varying thickness in an eccentric bearing as well.

For the simple case of a vertical shaft guided by a coaxial sleeve bearing, the following equation, derived from Newton's law of viscous flow, gives the power loss:[29]

$$H = 2\pi^3 \left(\frac{D}{C}\right)\left(\frac{L}{D}\right) ZN^2 D^3 \tag{1}$$

where H is the power loss, D is the diameter of the journal, C is the diametral clearance between the shaft and journal, L is the length of the journal, Z is the viscosity, and N is the speed in revolutions per unit time.

The coefficient of friction, f, is given by the equation:

$$f = 2\pi^2 \frac{D}{C}\frac{ZN}{P}, \tag{2}$$

where P is the load per unit of projected area.

Equation (2) is known as Petroff's law. Petroff's original equation included terms covering the effect of slip at the oil-metal boundaries. However, it was later shown that these effects do not exist.

Kingsbury[32] has developed an experimental method for studying hydrodynamic lubrication which is based upon the analogy between fluid and electrical flow. Wooden models are used, with a conducting liquid as the "lubricant". "Pressure" is measured as voltage and "flow rate" as current.

Bearings are designed for hydrodynamic lubrication whenever possible in order to take advantage of the low rate of abrasive wear and the low friction loss. The coefficient of friction in hydrodynamic lubrication is of the order of 0.001 to 0.01.[21] The lubrication of journal bearings is normally hydrodynamic, although boundary conditions may be present momentarily during starting and stopping. The lubrication of conventional internal combustion engines is largely hydrodynamic.[3]

Transition from Hydrodynamic to Boundary Lubrication

When the load on an oil film is increased or the viscosity or the speed decreased, the film decreases in thickness until a point is reached where the laws of hydrodynamics no longer apply, since the effects of surface or boundary forces are no longer negligible. As the film becomes still thinner, a state is ultimately reached where metal-to-metal contact is allowed. These transitions have a marked effect upon coefficient of friction, as shown in Figure 1, in which

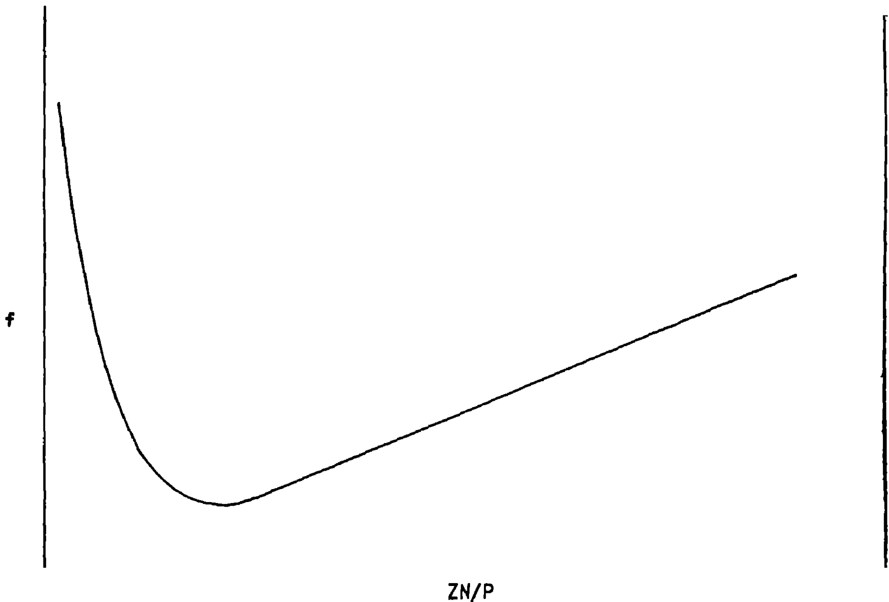


Figure 1. Coefficient of Friction, f, as a Function of Viscosity, Z; Velocity, N; and Pressure, P.

coefficient of friction is plotted as a function of the dimensionless parameter ZN/P, where Z, N, and P have the same meaning as in equation 2. According to equation 2 the coefficient of friction, f, is a linear function of ZN/P in the realm of hydrodynamic lubrication. Actually the experimentally determined values of f follow the theoretical values quite closely for high values of ZN/P As ZN/P decreases, the film thickness is reduced and the curve begins to deviate from linearity As ZN/P decreases further, a point is reached where both boundary and hydrodynamic effects prevail As ZN/P decreases

still further, the film ultimately ruptures and the curve shows a sharp upward break. The minimum point in the f vs. ZN/P curve is generally regarded as the transition point between fluid film, or hydrodynamic, and thin film, or boundary, lubrication. However, it must be understood that there is no sharp line of demarcation, but rather an intermediate zone in which both hydrodynamic and boundary effects are present between the two fields. This zone is sometimes called "semifluid", or "quasihydrodynamic".

"Stick-slip". When an elastically supported rider is borne on a slowly rotating disk, the motion of the rider with respect to the disk may be either continuous or intermittent. With low specific loads and thick films of lubricant, hydrodynamic conditions prevail and the motion is continuous. With unlubricated surfaces or with thin oil films the coefficient of friction is higher than in hydrodynamic lubrication. Furthermore the coefficient of kinetic friction is usually lower than the coefficient of static friction. Under these conditions the motion may be discontinuous, provided the elasticity is in the proper range. This is known as the "stick-slip" phenomenon.[12, 13, 13a, 87a, 89a] The rider moves with the disk when the instrument is started from a position of rest and continues to do so until the force required to move it equals a value determined by the coefficient of static friction. At this point the rider begins to move in the reverse direction with respect to the disk, since the coefficient of kinetic friction is lower than that of static friction. When it has moved back to a point where the drag is equal to a value determined by the kinetic coefficient of friction, it begins to move with the disk again, and the cycle is repeated. The frequency of the cycle may be very high. The temperature rise during the "slip" portion of the cycle may be high. Under such conditions the rate of abrasive wear is high.

Boundary Lubrication

Boundary lubrication, as mentioned earlier, covers a zone of thin film lubrication in which the laws of hydrodynamics play a negligible role. Blok[10] has proposed a classification of boundary lubrication on the basis of the mechanical conditions prevailing. He has listed the following main types:

Type 1. Low pressure and low temperature, or mild, boundary lubrication. Examples—Low speed sleeve bearings, leaf springs, hinge joints.

Type 2. High temperature boundary lubrication. Examples—Cylinders of superheated steam engines and internal combustion engines, especially aircraft engines, and certain high speed sleeve bearings.

Type 3. High pressure boundary lubrication. Examples—Cases involving rolling contact at high pressures but with little frictional or external heat, e.g., ball and roller bearings and certain spur gears.

Type 4. High pressure and high temperature, or extreme, boundary lubrication. Examples—Highly loaded hypoid or other gears characterized by high loads and a high degree of sliding friction, hence extensive generation of frictional heat and high local temperatures.

The temperature and pressure at the region of contact are the determining factors. Type 4, which is commonly called extreme pressure, or EP, lubrication, is discussed under a separate heading later in the chapter.

The property of lubricants which causes films of two oils of identical viscosity to exhibit differences in coefficient of friction is often referred to as "oiliness". Such differences can, by definition, not occur in hydrodynamic lubrication but are associated solely with the boundary state and the intermediate zone between the two states. While the phenomena occurring in the thin film or boundary state are not as thoroughly understood as hydrodynamic lubrication, a great deal of fundamental work has been done on boundary lubrication.

As mentioned earlier, the pressure in the oil film may be very high Viscosity-pressure coefficients, which are discussed in more detail in Chapter II, differ for different oils, and it has been shown by Everett[28] and by Givens[28] that differences in behavior in a high pressure journal between mineral oils of equal viscosity at atmospheric pressure can be explained on the basis of their viscosity at the pressure of the oil film. Thus some effects which might, for want of a clear understanding, be attributed to "oiliness" can actually be explained in terms of hydrodynamic lubrication if the effects of pressure and temperature upon viscosity are taken into account.

The coefficient of friction is of the order of magnitude of 0.1 in the boundary lubrication region.[46a] Beeck[5] has defined the boundary state as that in which the coefficient of friction is independent of viscosity and of sliding velocity. Pure boundary lubrication, as defined in this manner, is extremely rare in practice, since quasi-hydrodynamic effects are difficult to eliminate. Boundary lubrica-

tion is associated with forces acting at the boundary between oil and metal, and is therefore dependent upon both.[15, 47] An effective antifriction agent for one metal may be entirely ineffective for another. Bikerman[8a] attributes the effectiveness of boundary films to their high viscosity as compared to the viscosity of the bulk liquid.

When a surface is lubricated with a solid film of a compound such as a hydrocarbon, ketone, or normal alcohol, continuous sliding takes place. If the system is heated, a transition from continuous to stick-slip sliding occurs. The transition temperature is approximately equal to the melting point of the lubricant.[48, 26] With other lubricants, the transition temperature is appreciably higher than the melting point. Normal saturated acids, for example, show transition temperatures as much as 75°C higher than their melting points.[48]

Frewing[26] found that normal acids ranging from C_9 through C_{17} have transition temperatures about 70°C above their respective melting points. Conversion of the acid to the corresponding methyl ester lowers the transition temperature somewhat. The stearic acid esters of *n*-alcohols of varying molecular weight showed a different behavior. Esters of the lower alcohols had transition temperatures higher than their melting points, but the difference between the two temperatures decreased with increasing number of carbon atoms in the alcohol. The stearic acid ester of C_{10} *n*-alcohol behaved like a nonpolar compound in that the transition temperature and melting point were roughly equal.

When an oil oxidizes, the transition temperature often rises, since polar oxidation products are formed. A used oil may therefore be superior to the corresponding fresh lubricant as far as boundary lubrication properties are concerned.[24, 31] However, oxidation has many adverse effects upon the properties of an oil, and the formation of polar compounds by this means is usually accompanied by the simultaneous formation of sludge, lacquer, corrosive acids, and the like.

There is some question as to whether the interaction between metal and lubricant to form the boundary film is chemical or physical. Frewing[27] studied solutions of long-chain organic halides, esters, cyanides, thiocyanides, and nitro derivatives in white oil in a friction test run at high load and low speed He found that the transition

temperature, T_t, separating continuous from stick-slip sliding is related to the heat of adsorption, U, by the following equation:

$$\mathrm{Log}_e\, C = -U/RT_t + K, \tag{3}$$

where C is the concentration of polar material, R is the gas constant, and K is a constant. The transition was found to be reversible. Frewing concluded that the phenomenon is one of physical adsorption rather than chemical reaction. Bowden and coworkers, on the other hand, have shown in the case of oils containing fatty acids that the boundary lubrication of active metals such as zinc, cadmium, copper, and manganese is much more successful than that of unreactive surfaces such as glass, platinum, nickel, or chromium. This was taken as evidence that the effective film, instead of being physically adsorbed, is a chemical reaction product, viz., a soap of the fatty acid and the metal in question, formed by saponification of the acid with the metal oxide.[11] Regardless of whether the boundary layer is held to the metal by chemical or physical forces or a combination of the two, there can be no doubt that there is strong orientation of the polar molecules in the boundary film. This has been demonstrated conclusively by various investigators by electron diffraction and x-ray diffraction techniques.[42, 16, 1] Since the effect of polar compounds upon coefficient of friction is a surface phenomenon, minute concentrations of polar component are often sufficient. The effect of polar compounds, e.g , oleic acid, upon coefficient of friction caused by orientation at the boundary between oil and metal is analogous to the effect of polar compounds upon interfacial tension between water and nonpolar organic liquids and their ease of emulsification. In the latter case the polar compound orients at the boundary between water and nonpolar organic liquid. Low concentrations of appropriate polar compounds are effective in both cases.

A monomolecular layer of polar compound has a pronounced effect upon coefficient of friction under boundary conditions, but a thicker film is much more durable. This point is demonstrated strikingly in the following experiment, which was first performed by Langmuir:[34]

When a spherical glass rider is allowed to slide on a flat glass surface, the coefficient of friction can be reduced considerably if a monomolecular film of fatty acid is placed on the flat surface If, on the other hand, the monofilm is placed on the spherical rider,

the initial coefficient of friction will be reduced somewhat, but after the rider has moved a few millimeters the coefficient of friction returns to its original value. This was explained on the basis that in the first case the rider is constantly moving to an area of fresh film, whereas in the second the film is rapidly destroyed by the high local temperature produced at the area of contact.

With a monolayer on the flat surface it required 700 strokes of the rider to increase the coefficient of friction from 0.11 to 0.13, and an additional 200 strokes to increase it to 0.24. With an initial layer seven molecules thick the coefficient of friction did not change perceptibly in 4000 strokes. Beeck[5] has confirmed Langmuir's results. He found that a layer of polar compounds seven molecules thick wears almost indefinitely in an apparatus consisting of a friction pendulum equipped with either a four-ball bearing or a journal bearing on four balls.

Beeck has studied coefficient of friction for various lubricants as a function of angular velocity in the four-ball top, in which a single ball is rotated on a support formed by three stationary balls. He found that with built-up layers of certain polar compounds the coefficient of friction at first remains constant with increasing velocity, indicating boundary lubrication, and then suddenly drops at a definite and reproducible velocity. Since coefficient of friction is independent of velocity in the boundary region, the abrupt drop in coefficient of friction must mark a sudden transition into a quasi-hydrodynamic state. The effect was noticed only with built-up layers of several thicknesses of polar compounds which show well-oriented films by electron diffraction, and not with mineral oils free from polar components or with films only one or a few molecules thick. Beeck concluded therefore that a wedging effect induced by the adsorbed layer of polar molecules is responsible for the transition to quasi-hydrodynamic lubrication and the attendant drop in coefficient of friction.

EP Lubrication

As mentioned earlier, extreme boundary lubrication, in which both temperature and pressure are high, is commonly referred to as extreme pressure, or EP, lubrication. As Blok[10] has pointed out, the latter term is misleading, since temperature is a more decisive factor than pressure. The importance of temperature (resulting from friction at high speed) is illustrated in a statement by Mougey[41] to the effect that a spiral bevel gear lubricated with a mineral oil

could carry a load of 350,000 pounds at low speed but only 1,000 to 2,000 pounds at high speeds. However, the use of the terms "EP lubricant" and "EP lubrication" are so well established that it is very difficult to effect a change in terminology to the more logical expressions.

The development of EP lubricants was necessitated largely by the development of hypoid gears, which have certain mechanical advantages but which are very exacting in their lubrication requirements because of the high loads and the sliding velocities (hence high frictional temperatures) involved. EP lubricants are in widespread use, both in hypoid gears and in other types of gears and heavily loaded bearings.[22] EP lubricants are made by incorporating specific EP additives into a mineral oil base.

Beeck, Givens, and Williams[6] have made an interesting study of the mechanism of the action in oil solution of tricresyl phosphate and related compounds containing phosphorus or the related elements arsenic and antimony. They found that such compounds are quite effective in reducing wear* in the four-ball apparatus when balls consisting of metals which are capable of forming lower melting alloys with phosphorus, arsenic, or antimony, respectively, are used. With inert metals the additives are ineffective. From this they conclude that additives of this type actually form alloys at the local points of contact, where high temperatures prevail, and that the resulting flow of molten alloy results in a chemical polishing action, by which the load becomes distributed over a larger surface, thus decreasing pressures and temperatures. They found combinations of "chemical polishing agents" and long-chain polar agents, such as oleic acid, to be especially effective. This is attributed to the formation of an adsorbed film of the polar agent on the chemically polished surface.

As the load is progressively increased on a lubricated system, e.g., a set of gears, the oil film becomes progressively thinner. Abrasive wear increases under these conditions, and as the load is increased further a point is eventually reached where there is a welding together of portions of the two surfaces, followed by a tearing away of relatively large particles of metal. This type of failure is referred to as seizure, galling or scuffing. EP lubrication involves a chemical attack upon the surfaces where, as a result of high pressure, high

* Wear is discussed in greater detail in Chapter VII.

sliding velocity, and a rapid local generation of heat, the temperature has risen to a high figure. The formation of reaction products prevents seizure of the moving parts and may reduce friction. Since the temperatures involved may be very high (of the order of 500°C or higher in the case of steel on steel[9]), these reactions are often very rapid. The reaction is normally between an igredient of the lubricant and the metal. The performance of a given lubricant depends, therefore, upon the composition of the metal in the rubbing surface as well as upon the composition of the oil and the conditions to which the combination is subjected.

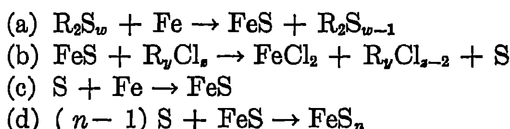
In the case of chlorinated and sulfurized EP dopes the mechanism has been quite well established as consisting of the formation of an inorganic film. Baxter, Snow, and Pierce[4] showed that pretreatment of the test pieces with chlorinated or sulfurized EP dope at elevated temperatures or with hydrochloric acid resulted in a considerable increase in breakdown load in both the four-ball and the Timken tests.

Davey[20] found that pretreatment of the test pieces used in the four-ball apparatus with free sulfur or with ammonium sulfide, both of which gave sulfide films, resulted in families of friction-time curves for straight mineral oils, at least until the sulfide film was worn away, similar to those obtained when a sulfur-containing EP oil is run with untreated steel balls.

Simard, Russell, and Nelson[45] have studied the film-forming action of lead naphthenate and free sulfur, both singly and in combination, by means of electron diffraction patterns. They allowed the films to form either by heat treatment under static conditions or by friction in the SAE machine or in gears. Various base stocks and base stocks plus free sulfur showed the presence of oxides of iron on the surface after exposure to heat. The addition of lead naphthenate to the base stock resulted in the formation of an amorphous film on the surface. This was believed to be either lead naphthenate itself or its oxidation product. Lubricants containing both free sulfur and lead naphthenate formed an initial film of lead sulfate, with lead sulfide forming later. The surface of hypoid gears which had been run for 20,000 miles on this lubricant showed the presence of iron oxide plus a phase which was believed to be a lead-rich sulfide of lead. Simard, Russell, and Nelson believe that the chemical polishing theory of Beeck, Givens, and Williams may apply in the case of lead-sulfur

lubricants as well as to the phosphorus type lubricants for which the theory was proposed. The presence of lead sulfate and iron oxide indicates that oxidation is involved in the chemistry of EP lubricants of this type.

Prutton, Turnbull, and Dlouhy[44] have studied the mechanism of lubrication by EP lubricants containing both sulfur and chlorine. They analyzed the surface films formed on hypoid gears during "shock" testing in an automobile and found both ferrous chloride and iron sulfide. They postulate either a direct reaction between iron and the additive to form iron chlorides and iron sulfide, respectively, or a preliminary decomposition of the additive to HCl in the case of the chlorine additive and H_2S in the case of the sulfur dope. Their data indicate that intermediate formation of HCl and H_2S are probably not a part of the mechanism, although both are formed in the reaction. They found that in general an iron sulfide film will be formed from an active sulfur additive more rapidly than an iron chloride film forms from an active chlorine additive when either is present alone. However, when both are present simultaneously, considerably more ferrous chloride is formed than would be expected from the individual behavior of the two additives. This indicates that the chlorine additive reacts more rapidly with iron sulfide than with iron itself. On the basis of their data as a whole, Prutton *et al.* have postulated the following mechanism for the joint behavior of active sulfur and active chlorine additives on iron:



(a) $R_2S_w + Fe \rightarrow FeS + R_2S_{w-1}$
(b) $FeS + R_yCl_z \rightarrow FeCl_2 + R_yCl_{z-2} + S$
(c) $S + Fe \rightarrow FeS$
(d) $(n-1)\,S + FeS \rightarrow FeS_n$

Types of EP Lubricants. Hundreds of compounds and mixtures have been patented as EP dopes, antifriction agents, film strength improvers, etc An exact classification is difficult, since many complex mixtures are patented. However, it is possible to group most of them into the following six main classes according to their functional groups:

(1) *Organic compounds containing oxygen.* This includes various carboxylic acids, esters, ketones, and oxidized petroleum fractions. Members of this group act mainly by adsorption or, as Bowden has shown in the case of fatty acids and active metals, through the

formation of a soap film. Their use is restricted to mild conditions.

(2) *Organic compounds containing sulfur or combinations containing oxygen and sulfur.* Many synthetic organic compounds as well as reaction products of free sulfur and petroleum fractions or various organic compounds are included in this group.

(3) *Organic compounds containing chlorine.* Practically all the members of this group are made by chlorinating either organic compounds or petroleum fractions.

(4) *Organic compounds containing both chlorine and sulfur or mixtures of chlorine compounds and sulfur compounds.* Many are combinations of compounds listed individually under the previous two classes, while some, e.g., those made by reacting a hydrocarbon or mixture of hydrocarbons with sulfur chloride, contain both active groups in the same molecule.

(5) *Organic compounds containing phosphorus.* Both trivalent and pentavalent phosphorus compounds are included. As discussed earlier, these compounds act through their chemical polishing effect rather than as anti-welding agents.

(6) *Organic compounds containing lead.* Lead naphthenate is the compound normally used in conjunction with either an active sulfur or an active chlorine additive.

Test Methods. Several bench tests have been developed for the evaluation of EP lubricants. All these tests are similar in that two well-defined surfaces, separated by a film of lubricant, are involved, with one or both in motion. The load is normally increased in a stepwise fashion, and the maximum allowable load before seizure occurs is measured Since the various tests differ in such factors as design and composition of test specimens, temperature, speed, and rate of loading, they do not necessarily rate a given series of lubricants in the same order. Some correlate better with one type of service requirement, and others with another. Five of the more commonly used bench tests (the operating principles of which are illustrated in Figure 2) are briefly described below:*

(1) *Timken.*[25, 39, 48, 53] A steel block is pressed against a rotating cylindrical steel ring for a period of ten minutes. The highest load at which no seizure occurs is recorded. CRC (Coordinating Research Council) test No. L-18-545 employs the Timken machine.

(2) *Almen.*[41, 51] A cylindrical rod is rotated in a split bushing

* All these tests are conducted under dynamic conditions. They do not measure starting torque, which is essentially a static phenomenon.

which is pressed against it. Two-pound weights are added at ten-second intervals, and the results are expressed in a manner similar to that used in the Timken test.

(3) *Falex.*[19, 38] A cylindrical rod is rotated between two hard V-shaped bearing blocks which are pressed against the rod with progressively increasing pressure. Since most of the wear occurs on the softer shaft, the area of contact and hence the specific pressure

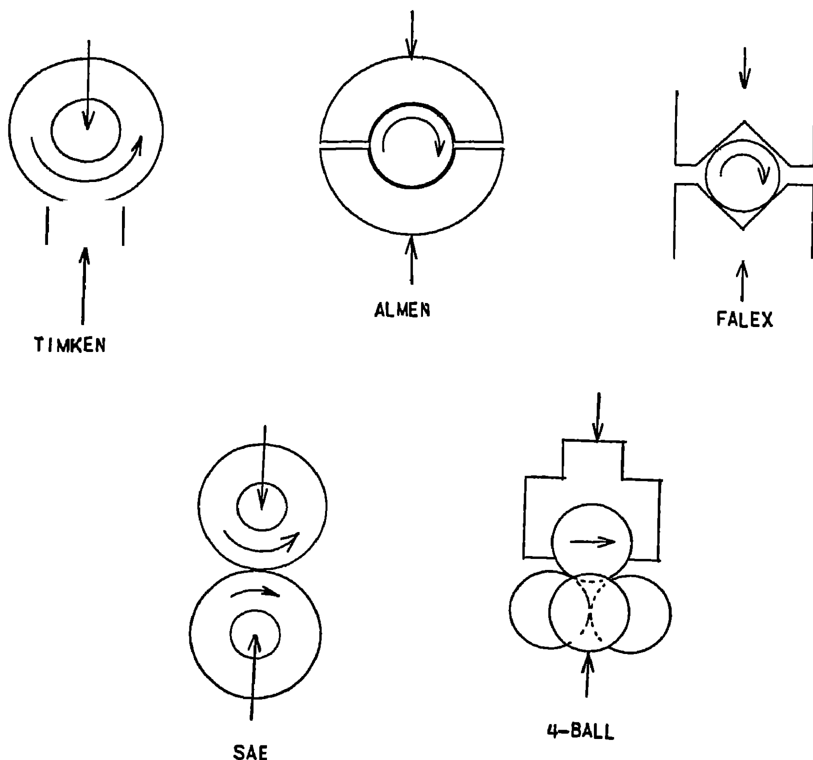


Figure 2 Operating Principles of Various Bench Tests for Lubricants

at the area of contact remains essentially constant as wear proceeds. Total load and torque are indicated on gauges.

(4) *Four-ball* [9, 48, 17, 18, 30] A half-inch steel ball is rotated in contact with three similar balls which are clamped in a stationary position. This provides three points* of contact in contrast to the line*

* It should be understood that the terms "point contact" and "line contact" are used for the sake of simplicity and are not geometrically correct. The region of contact is actually an area in both cases; circular in the former, and rectangular in the letter.

contact existing in the other test machines. Wear and coefficient of friction can be measured, and the test may be run at increasing loads until the heat generated by friction welds the balls together.

(5) *SAE.*[48, 87, 88] Two cylinders, which are driven at different speeds, are rotated against each other. The load is increased until failure occurs This machine differs from the four mentioned above

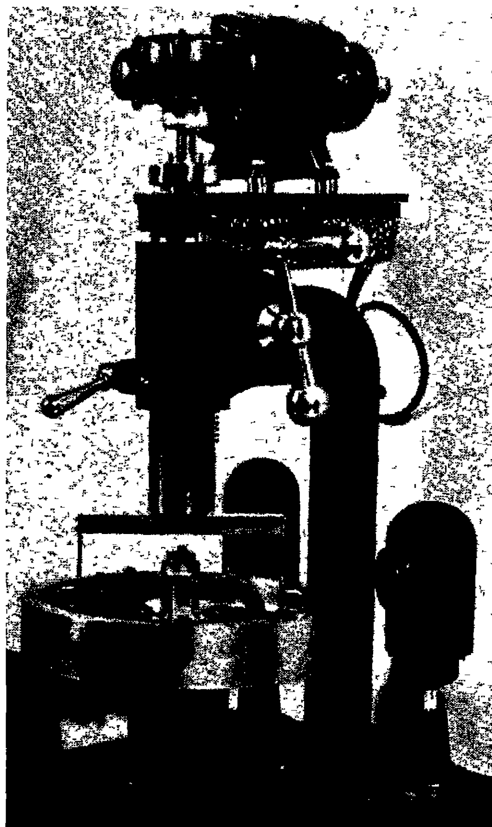


Figure 3. Four-ball Apparatus.

in that it provides a combination of rolling and sliding friction on both test pieces, i.e., the line of contact is constantly changing, whereas in the other machines it remains fixed on the stationary member. The ratio of sliding to rolling friction can be changed by varying the relative speed of the two cylinders. CRC test No. L-17-545 employs the SAE machine.

Good correlation with gear tests in automotive equipment is claimed for both the SAE test[37, 38, 54] and the four-ball test.[9, 30, 36] Blok[9] compared the behavior of several EP lubricants in the four-ball, the SAE, and the Timken tests with their performance in a Chevrolet hypoid gear at 40 mph. He found that the four-ball test gives the best criterion of performance in this particular application, the SAE test next, and the Timken the poorest of the three. Correlation of any of these tests with performance in practice depends to a large extent upon the conditions prevailing in practice and upon those chosen for the test. It is possible to vary the conditions over a considerable range in each of the tests.

The 1946 CRC Handbook published by the Coordinating Research Council describes two full-scale tests which are used in the evaluation of gear oils. CRC Designation L-19-645 is a procedure for determing the load-carrying characteristics of gear oils in axles under conditions of high speed and light loads. It is run in the hypoid assembly of a passenger car. The test may be run either on the road or on a chassis dynamometer. CRC Designation L-20-545 covers a test procedure for determining the load-carrying, wear, stability, and corrosion characteristics of gear lubricants in axles under conditions of high torque and low speed. Mild boundary lubricating properties are probably of more importance than the conventional EP properties in this test. The test is run in the hypoid rear-axle carrier of a $\frac{3}{4}$ ton Army truck on a dynamometer test stand.

Oleophobic Films

Fatty oils have lower interfacial tension values against water and against metals than mineral oil. It might therefore be expected that fatty oils would show the greater affinity for metals and hence the greater tendency to spread on metal surfaces. However, it has been shown by Bulkley and Snyder[14] that when a drop of olive oil is placed on a clean steel surface it remains standing at a high contact angle, while a drop of mineral oil spreads into a thin film. Furthermore, if a drop of fatty oil is rolled across a clean steel plate and the plate then dipped into mineral oil and allowed to drain, the mineral oil remains in a film on the portions which were originally clean, but runs off the portions which had been in contact with the fatty oil.

This behavior is explained on the basis of an adsorbed oriented

film of polar molecules which lower the surface tension of the solid to such an extent that spreading is not favored on the new surface. Woog[52] found that dibasic acids have an even greater effect than monobasic acids in preventing the spreading of mineral oils on metal surfaces.

Bigelow, Pickett, and Zisman[8] and Bigelow, Glass and Zisman[7] have made a systematic study of oleophobic films adsorbed from solutions in nonpolar liquids. They found that the effective film is a well oriented monolayer, formed by reversible adsorption from solution. They concluded that the films are composed of almost vertically oriented, close-packed molecules with the polar group attached to the metal. The outer layer of the monomolecular film consists of methyl groups. Polar molecules having a configuration corresponding to a long rod or flat plate, with the polar group at one extremity and one or more methyl groups at the other, satisfy this requirement. If a double bond is present in the molecule as in oleic acid, no oleophobic film is formed. This has been explained on the basis that adsorption takes place at both the polar group and the unsaturated bond, and the molecule is not adsorbed vertical to the surface, but more nearly horizontally.

The equilibrium between dissolved and adsorbed polar compound for a given solvent and solid depends to a large extent upon the polar group. Bigelow, Pickett, and Zisman found that oleophobic films were formed on platinum and pyrex from weight per cent concentration of only 10^{-7} in the case of primary aliphatic amines and monocarboxylic acids, while a concentration of 10^{-4} was required for aliphatic alcohols, esters, and ketones.

Oleophobic films are desirable in timepieces and other instruments since they prevent excessive spreading or "creeping" of the lubricant. Various compositions claimed to show a minimum tendency to spread have been patented for this purpose.[2, 36a, 40, 50]

These oleophobic films are also highly hydrophobic[7, 8] and polar compounds capable of forming such films are used as rust preventives. This is discussed further in Chapter VII.

Bibliography

1. Andrew, L. T., *Trans. Faraday Soc.*, **32**, 607–16 (1936).
2. Barker, G. E., U. S. Patent 2,355,616 (1944).
3. Barnard, D. P., and Barnard, E. P., *Refiner and Natural Gasoline Mfr*, **14**, 324–8 (1935).
4. Baxter, J. P., Snow, C. I., and Pierce, T. T., *J. Inst. Petroleum*, **25**, 761–70 (1939).

5. Beeck, O., *J. Applied Phys.*, **12**, 512–18 (1941).
6. Beeck, O., Givens, J. W., and Williams, E. C., *Proc. Roy. Soc.* (*London*), **A177**, 103–18 (1940).
7. Bigelow, W. C., Glass, E., and Zisman, W. A., *J. Colloid Sci.*, **2**, 563–91 (1947).
8. Bigelow, W. C., Pickett, D. C., and Zisman, W. A., *J. Colloid Sci.*, **1**, 513–38 (1946).
8a. Bikerman, J. J., *Lubrication Eng.*, **4**, 208–14 (1948).
9. Blok, H., *2 me Congr. mondial pétrole*, **3**, Sect. 4, 471–86 (1937), *Inst. Mech. Engrs.*, "General Discussion on Lubrication", Vol. **2**, 14–20 (1937).
10. Blok, H., *S.A.E. Journal*, **46**, 54–68 (1940).
11. Bowden, F. P., Gregory, J. N., and Tabor, D., *Nature*, **156**, 97–101 (1945).
12. Bowden, F. P., and Leben, L., *Proc. Roy. Soc.* (*London*), **A169**, 371–91 (1939).
13. Bowden, F. P., Leben, L., and Tabor, D., *Trans. Faraday Soc.*, **35**, 900–5 (1939).
13a. Bowden, F. P., and Tabor, D., "The Friction and Lubrication of Solids", Oxford at the Clarendon Press, 1950
14. Bulkley, R., and Snyder, G. H. S., *J. Am. Chem. Soc.*, **55**, 194–208 (1933).
15. Charron, F., *Pub. sci. et tech. ministère air* (*France*), No. 169 (1940); *Chem. Abstracts*, **35**, 7166 (1941).
16. Clark, G. L., Sterrett, R. R., and Lincoln, B. H., *Ind. Eng. Chem.*, **28**, 1318–28 (1936).
17. Clayton, D., *J. Inst. Petroleum*, **26**, 256–71 (1940).
18. Clayton, D., *Inst. Mech. Engrs.*, "General Discussion on Lubrication", Vol. **2**, 34–42 (1937).
19. Crowley, C. A., and Faville, F. A., Paper presented before Sectional Regional Meeting of S.A.E., Chicago, Sept. 29–Oct. 1, 1937.
20. Davey, W., *J. Inst. Petroleum*, **31**, 154–58 (1945).
21. Dawkins, A. E., *Australian Chem. Inst. J. & Proc.*, **2**, 41–50 (1938).
22. Evans, E. A., *Inst. Mech. Engrs.*, "General Discussion on Lubrication", Vol. **2**, 55–59 (1937).
23. Everett, H. A., *S.A.E. Journal*, **41**, 531–37 (1937)
24. Exline, P. G., Kramer, W. E., and Bowman, J. R., *J. Inst. Petroleum*, **29**, 295–307 (1943).
25. Frame, A. P., and Graham, A. K., *Oil Gas J.*, **31**, No. 33, 14, 16 (1933)
26. Frewing, J. J., *Proc. Roy. Soc.* (*London*), **A181**, 23–42 (1942).
27. Frewing, J. J., *Proc. Roy. Soc.* (*London*), **A182**, 270–86 (1944).
28. Givens, J. W., *Ind. Eng. Chem.*, **31**, 1135–38 (1939).
29. Hersey, M. D., "Theory of Lubrication", New York, John Wiley and Sons, (1938).
29a. Kalichevsky, V. A., *Petroleum Refiner*, **28**, 121–6 (1949).
30. Kemmerer, H. R., and Garton, F. L., *Nat. Petroleum News*, **31**, R551–5 (1939).
31. King, E. O., *Proc. Roy. Soc.* (*London*), **A139**, 447–59 (1933).
32. Kingsbury, A., *Applied Mechanics, Trans. Am. Soc. Mech. Engrs.*, **53**, 59–75 (1931)
33. Kyropoulos, S., *Refiner Natural Gasoline Mfr.*, **18**, 320–24 (1939).
34. Langmuir, I., *J. Franklin Inst.*, **218**, 143 (1939).
35. Lincoln, B. H., Byrkit, G. D., and Steiner, W. L., *Ind. Eng. Chem.*, **28**, 1191–97 (1936)
36. Mansion, H. D., *Engineering*, **154**, 138–40 (1942).
36a. Martin, J. S., U. S. Patent 2,534,611 (1950).
37. McKee, S. A., Bitner, F. G., and McKee, T. R., *S.A.E. Journal*, **32**, 402–8 (1933)
37a. Merchant, M. E., *Lubrication Eng.*, **2**, 56–62 (1946)
38. Miller, F. L., *Inst. Mech. Engrs.*, "General Discussion on Lubrication," Vol. **2**, 107–17 (1937).
39. Mikita, J. J., *Steel*, **115**, No. 11, 102–4, 148–54 (1944).

39a. Morgan, F , Muskat, M , and Reed, D W , *Lubrication Eng.*, **5**, 75–82, 103 (1949).
40. Morgan, J. D., and Lowe, R. E , U. S. Patent 2,423,844 (1947).
41. Mougey, H. C., *Proc. 15th Ann. Meeting Am. Petroleum Inst.*, **15**, Sect. III, 60–8 (1934); *Oil Gas J.*, **33**, No. 26, 123, 126–8 (1934).
42. Murrison, V A., *Phil. Mag.*, **17**, 201–25 (1934).
43. Norton, A. E , "Lubrication", New York and London, McGraw-Hill, (1942).
44. Prutton, C. F , Turnbull, D., and Dlouhy, G., *J. Inst Petroleum*, **32**, 90–118 (1946).
44a Sellei, Helen, *Petroleum Processing*, **4**, 1116–20 (1949).
45. Simard, G. L , Russell, H. W., and Nelson, H. R., *Ind. Eng. Chem.*, **33**, 1352–9 (1941).
46. Tabor, D., *Nature*, **147**, 609–10 (1941).
46a. Thorpe, R. E., and Larsen, R. G., *Ind Eng. Chem.*, **41**, 938–43 (1949).
47. Trillat, J. J., *Rev gen. sci.*, **48**, 95–107 (1937), *Chem. Abstracts*, **31**, 4479 (1937).
48. van der Minne, J. L., *Inst. Mech. Engrs.*, "General Discussion on Lubrication", Vol. **2**, 429–41 (1937).
49. Vineall, G. J. C., *Petroleum (London)*, **6**, 61–2 (1943).
50 Wasson, J I , and Zimmer, J. C., U. S. Patent 2,417,281 (1947).
51. Wolf, H. R., and Mougey, H. C., *Proc. Am Petroleum Inst* , **13**, Sect. III, 118–31 (1932); *Oil Gas J* , **31**, No. 26, 58–61 (1932)
52. Woog, P., *Compt. rend.*, **189**, 977–9 (1929).
53. Wooler, E., *S A.E. Journal*, **28**, 53–60 (1931).
54. Zwahl, C. E , *S.A.E. Journal*, **41**, 555–65 (1937).

Chapter II

RHEOLOGY

Introduction

The importance of the internal flow resistance or viscosity of a lubricant has already been discussed in Chapter I. Viscosity is defined by Newton's law which states that at a given point in a fluid the shearing stress, S, is directly proportional to the rate of shear, R,

$$S = \eta R, \tag{4}$$

The proportionality constant, η, is known as the coefficient of viscosity. Since for the motion of two parallel layers of liquid the shearing stress is equal to F/A, where F is the force and A the area, and since the rate of shear is equal to v/d, where v is the velocity and d the distance between the layers, equation (4) may be written:

$$\frac{F}{A} = \eta \frac{v}{d}, \tag{5}$$

or,

$$\eta = \frac{Fd}{Av} \tag{6}$$

Poiseuille has shown that the flow of liquids in capillary tubes is governed by the equation:

$$\eta = \frac{\pi P r^4}{8Vl} t, \tag{7}$$

where P is the pressure, r the radius of the tube, l the length of the tube, and V is the volume of liquid flowing in time t.

If two parallel liquid surfaces of unit area and separated by unit distance slide past each other at unit velocity, the viscosity of the liquid is defined as unity. The metric unit of viscosity is the *poise*, named in honor of Poiseuille. Water at 20°C or 68°F has a viscosity of approximately 0.01 poise, or one centipoise. Thus the viscosity of a liquid in centipoises indicates its relative viscosity compared to water at room temperature. The corresponding English unit of

viscosity is the *reyn*, named in honor of Reynolds. Poises (dyne-seconds per square centimeter) may be converted to reyns (pound-seconds per square inch) by dividing by 68,950. The name *newton* is sometimes used for a more practical unit of one millionth of a reyn. Since one centipoise = 0.01 poise and since one poise = 1/68,950

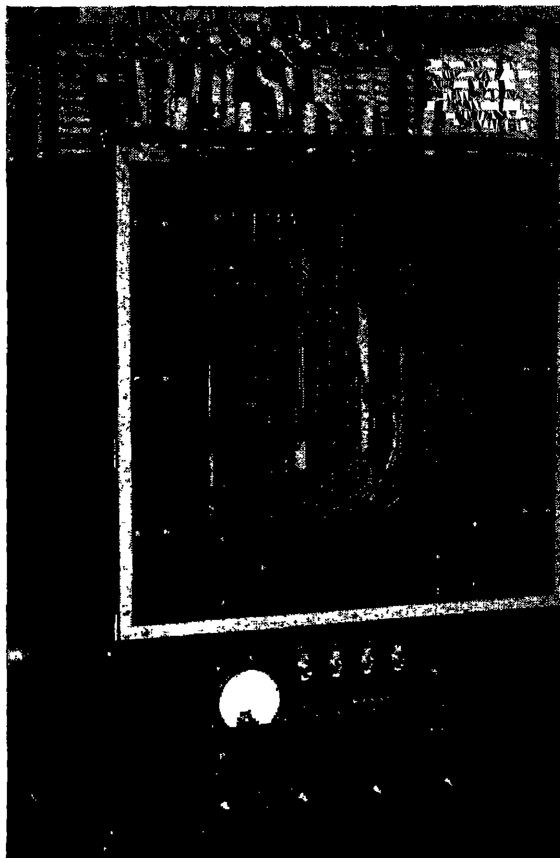


Figure 4. Capillary Viscometers and Bath

reyn, it follows that one newton = 6.895 centipoises. Neither the reyn nor the newton is commonly used.

There are various capillary tube viscometers, including the Ostwald, the Ubbelohde, the Vogel-Ossag, and the Fitz-Simons, for determining viscosity experimentally. Other viscometers include the falling ball and the rotating drum types.

In addition to the units of viscosity defined above there are several related units in common use in the petroleum industry. The most fundamental of these is the kinematic viscosity, which is defined as viscosity divided by density. The unit of kinematic viscosity is the *stoke* (stokes = poises/density), and the common practical unit the *centistoke*. The viscosity of lubricants is often expressed in terms of arbitrary units based on industrial viscometers, the most common of which are the Saybolt, the Redwood, and the Engler. The relationship between the various viscosity units is not linear. Barnard[7] has published an extensive conversion table which includes kinematic viscosity (centistokes), Saybolt Universal, Saybolt Furol, Redwood No. 1, Redwood No. 2, and Engler. The relative magnitudes of the various scales is illustrated in Table 1. It will be observed that the conversion to Saybolt Universal or to Redwood No. 1 depends to a certain degree upon the temperature.

TABLE 1. COMPARISON OF VARIOUS VISCOSITY UNITS

Centistokes	75.0
Stokes	0 75
Saybolt Universal Seconds, 100°F	345 6
Saybolt Universal Seconds, 210°F	349.3
Saybolt Furol Seconds	35 8
Redwood No 1 Seconds, 70°F	304
Redwood No 1 Seconds, 140°F	306
Redwood No. 1 Seconds, 200°F	312
Redwood No 2 Seconds	31 8
Engler degrees	9 88

Motor lubricants are conveniently classified according to their viscosity. The SAE (Society of Automotive Engineers) classification is commonly used for this purpose. The SAE system is defined in Table 2 This system is a revision, adopted in 1950, of an earlier classification which had been in use for some time.

Viscous and Turbulent Flow

Liquids which flow in accordance with Newton's law are known as Newtonian liquids Flow of this type is known as viscous or streamline flow. The viscosity, or the ratio of shearing stress to rate of shear, is constant for Newtonian liquids flowing under these conditions. Most lubricating oils behave very nearly like Newtonian liquids at the temperatures, pressures, and flow rates ordinarily encountered. However, as the flow rate is increased, the ratio of shearing stress to rate of shear suddenly decreases at a critical point.

This point marks the transition between viscous flow, in which the liquid follows Newton's law, and turbulent flow, in which the liquid no longer behaves in Newtonian fashion Viscous flow consists of an orderly motion in which layers of liquid slide past one another in a direction parallel to the direction of flow. In turbulent flow, on the other hand, the motion is erratic. Reynolds has shown that the critical velocity separating viscous from turbulent flow through a pipe depends upon the dimensionless function DuP/η, where D is the inside diameter of the pipe, u is the velocity of the liquid, and P and η the density and viscosity, respectively, of the liquid. The expression DuP/η is known as the Reynolds number. When the Reynolds number is low the flow is viscous. The transition normally occurs between values of 2,100 and 4,000, depending upon the design of the pipe.

TABLE 2 SAE CLASSIFICATION OF MOTOR LUBRICANTS

SAE Number	Viscosity Range, Saybolt Universal			
	0°F		210°F	
	Min	*Max.*	*Min.*	*Max.*
5w		4000	59	
10w	6000[a]	12000	39	
20w	12000[b]	48000	39	
20			45	58
30			58	70
40			70	85
50			85	110

[a] Minimum at 0°F may be waived if viscosity at 210°F is not below 40.
[b] Minimum at 0°F may be waived if viscosity at 210°F is not below 45.

Viscosity is a less important factor in turbulent than in viscous flow. For example, if two liquids of identical density but having viscosities differing by a factor of ten are pumped at the same velocity through identical pipes of such a diameter and at such a velocity that the Reynolds number is 100 and 1000, respectively, the flow will be viscous in both cases and the pressure drop across a given length of pipe will be ten times as great in the case of the liquid of greater viscosity (lower Reynolds number) If, on the other hand, the diameter of the pipe and the velocity are increased so that the Reynolds number is 10,000 and 100,000, respectively, the flow will be turbulent in both cases and the pressure drop per unit length of pipe will be less than twice as great for the more viscous liquid than for the less viscous one.

Flow of Lubricating Greases

Most lubricating greases are plastic solids. Such substances differ from Newtonian liquids in their flow characteristics in two respects: (1) the curve relating rate of shear, R, to shear stress, S, passes through the origin in the case of liquids, i.e., an infinitesimal shear stress results in flow. The plastic solid, on the other hand, requires a definite stress before flow begins. (2) The R vs. S curve is linear for Newtonian liquids, while for plastic solids it is generally not linear.

The viscosity of a grease at a given temperature and pressure cannot be described in a single number, but may be expressed as a function of the rate of shear. Most of the instruments for measuring viscosity are inadequate for the evaluation of greases either because of the complex function of shear involved or because they can be used only with very fluid greases. Furthermore most of them operate at far too low a range of rate of shear to be useful for predicting fluid film lubrication. Arveson[2, 3] made an extensive study of this problem and worked out a "constant-shear viscometer" in which a grease is forced through a calibrated capillary at a constant rate. A piston forces hydraulic fluid into a cylinder which contains a second piston. As the piston moves, it forces the grease sample through the capillary. From the speed of the driving mechanism, the dimensions of the system, and the pressure of the hydraulic fluid as measured by a gage, it is possible to calculate the apparent viscosity at the particular temperature and shear rate involved. The Poiseuille equation is used in this calculation:

$$\eta_\alpha = \frac{\pi P R^4}{8LV/t} = \frac{\dfrac{PR}{2L}}{\dfrac{4V/t}{\pi R^3}} = \frac{F}{S}, \tag{8}$$

where η_α = apparent viscosity (poises); P = pressure (dynes/cm^2); R = radius of capillary (cm); L = length of capillary (cm); V/t = rate of efflux (cm^3/sec); F = stress (dynes/cm^2); and S = rate of shear (sec^{-1}). Apparent viscosity is defined as being equal to the viscosity of a Newtonian liquid which would flow at the same rate as the grease under the same conditions.

Blott and Samuel[9] have pointed out the fact that the true viscosity of a non-Newtonian fluid can be calculated from the experimental data obtained from a pressure viscometer of the capillary tube type

whitout making use of the assumptions necessary if the Poiseuille equation is to be applied to such a material. The equation they used is the following:

$$\frac{d(Q/\pi R^3)}{dF} = \frac{1}{\eta} - \left(\frac{3}{F}\cdot\frac{Q}{\pi R^3}\right), \tag{9}$$

where η is the absolute viscosity in poises, Q is the rate of efflux, V/t, and the other symbols have the same meaning as above. The two equations do not appear to give widely different results when applied to the same data, at least in the case of the data presented by Blott and Samuel.

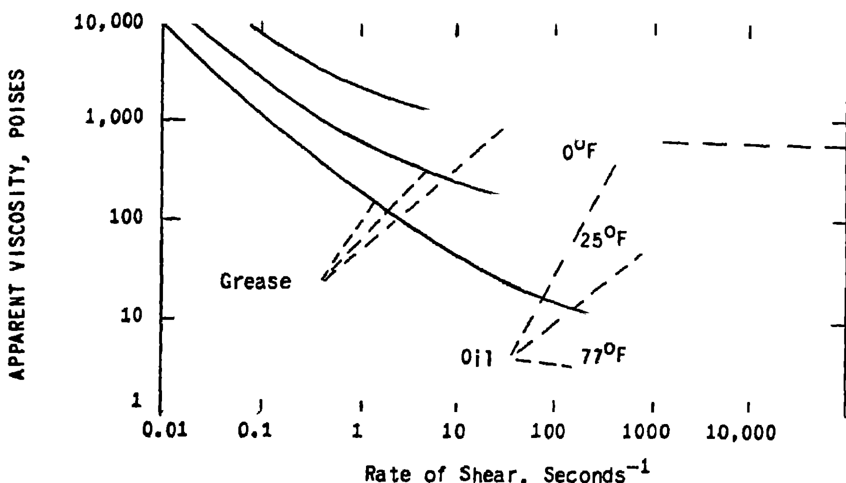


Figure 5. Isotherms for a Typical Calcium Soap Grease and the Petroleum Oil Contained Therein. (Taken from Arveson[3])

Arveson[3] has shown that the apparent viscosity of a grease at a given temperature is determined by rate of shear, the viscosity of the oil, and a "soap factor," K, which appears to be a function primarily of the soap content of the grease. He found that it was possible to express the apparent viscosity of a series of calcium base greases as a function of these three variables He expressed the belief that a general curve exists for each type of soap but that the relation involved can not be expressed in the form of a simple mathematical equation. Hence the data are usually expressed in the form of curves in which apparent viscosity is plotted against the rate of shear. Typical curves are shown in Figures 5 and 6. The data are plotted

logarithmically, and very wide ranges of rate of shear and viscosity are covered. It will be observed that the apparent viscosity of a grease decreases rapidly with increasing rate of shear and approaches, although it never equals, the viscosity of the mineral oil component of the grease at high rates of shear. It is this dependence of apparent viscosity upon rate of shear which distinguishes grease from oil and which enables the former to lubricate without excessive "drag" at high speeds while possessing sufficient "body" to remain in the housing during periods of shutdown. Increasing soap content increases the apparent viscosity, particularly at low rates of shear. According

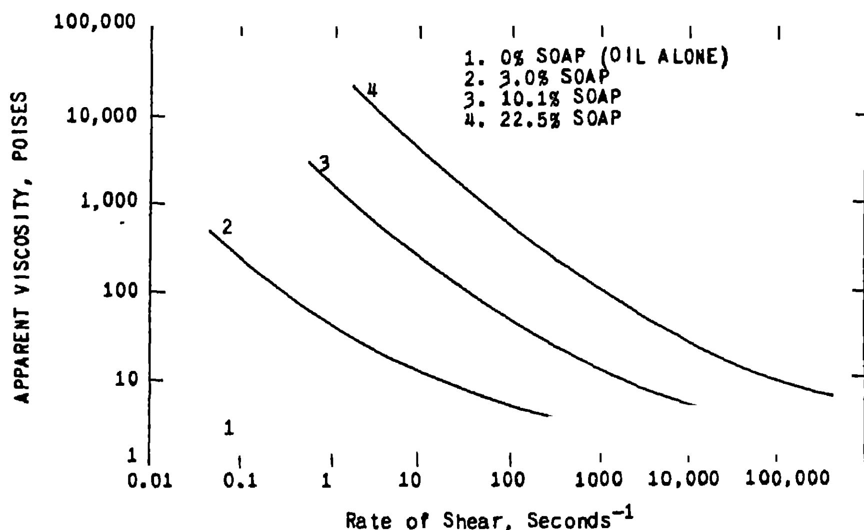


Figure 6 Apparent Viscosity vs. Rate of Shear for Cup Greases of Different Soap Content. (Taken from Arveson[3])

to Arveson,[3] "Low rates of shear are involved in dispensing of lubricants, approximately 0.1 to 1000 reciprocal seconds, while leakage from housings and feeding from boxes and cups involves an even lower range. Fluid film lubrication involves rates of shear from 10,000 reciprocal seconds to indefinitely large values." Thus a family of curves similar to those shown in Figure 5 and covering a temperature range including the lowest starting temperature and the highest operating temperature for a given mechanism can be of extreme value in evaluating the grease to be used in the mechanism.

The Standard Oil Development Company, or SOD, viscometer[6]

is a modification of the Arveson instrument. It was designed for simplicity and flexibility of operation and is in fairly general use.

Amner and Blott[1] have described two additional instruments for determining the rheological properties of grease and other soft solids. The one is a "plunger" instrument in which the grease is placed inside a cylindrical container which is closed at one end. A solid cylindrical plunger, slightly smaller in diameter than the inside diameter of the outer cylinder, is forced into the grease by applying a known load. From the dimensions of the apparatus, the load applied, and the rate of travel of the plunger, the apparent viscosity can be calculated. The instrument is designed to cover rates of shear of the order of zero to 1,000 reciprocal seconds. The other instrument described by Amner and Blott is a pendulum device in which a rectangular block, carried at the end of a pendulum arm, is allowed to swing between parallel plates which are arranged so that the space between the plates and the block is small. This space is filled with a film of grease. The calculation of viscosity is based on the energy lost by the pendulum as it passes through the grease, the thickness of the grease film, and the velocity of the pendulum. Higher rates of shear, of the order of 50,000 reciprocal seconds, are attainable with this instrument.

Pour Point

The pour point of an oil is defined as the lowest temperature at which the oil will flow when chilled under specified conditions. It is somewhat higher than the "solid point." It is difficult to define either pour point or solid point precisely, since the transition from liquid to solid is a gradual one. The cloud point is defined as the temperature at which wax or other dissolved solids first precipitate during chilling under specified conditions.

The pour point may mark the temperature at which crystallization of wax has proceeded to such an extent that a further lowering of temperature would cause flow to cease ("wax pour point") or it may, in the case of wax-free oils, represent the temperature at which the viscosity is so high that further cooling with the attendant further increase in viscosity, causes flow to stop ("viscosity pour point"). Oils which are free from wax or other components which precipitate on chilling behave like Newtonian liquids even at very low temperatures. The viscosity at the pour point should be the

same for all liquids of this type. This viscosity is of the order of 10^5 to 10^6 centistokes. Velikovskii[27] reports the viscosity at the pour point for oils which set in a "viscous manner" to range from 2,000 to 6,000 poises. This would correspond roughly to 2×10^5 to 6×10^5 centistokes. Hennenhöfer,[21] on the other hand, reports a value of 3×10^6 centistokes. As mentioned previously, pour point cannot be defined precisely, and the viscosity at the pour point can be defined with even less precision since a small difference in temperature corresponds to a large difference in viscosity in this range.

Most commercially used lubricating oils show a "wax pour point" rather than a "viscosity pour point." Such oils behave as Newtonian liquids only at temperatures above the point at which wax begins to separate, i.e., above the cloud point. Below the cloud point the viscosity of the system is a function both of the viscosity of the liquid and the effect of the suspended particles Einstein has shown that the viscosity of a dilute suspension of rigid spheres in a viscous liquid is given by the equation:

$$\eta = \eta_0 (1 + 2.5 \phi), \tag{10}$$

where η is the viscosity of the suspension, η_0 is the viscosity of the liquid phase, and ϕ is the ratio of the volume of disperse phase to the volume of suspension. As the oil is chilled further the wax crystals increase both in size and in number until a point is reached where the crystals interlock and prevent free flow. At this point the viscosity is dependent upon the rate of shear in much the same manner previously shown for lubricating grease.

The "wax pour point" is dependent upon such factors as rate of cooling and degree of agitation as well as upon the type of wax and pour point depressant present, and their concentrations.

ASTM Method D97 for the determination of pour point specifies that the sample be maintained at a temperature of 115°F or lower for at least 24 hours prior to the test.[5] The sample is then cooled systematically under quiescent conditions and observed at intervals of 5°F. The pour point is the lowest temperature at which the oil flows when the container is tilted. This is known as the upper or maximum pour point. If the sample is heated, e.g., to 220°F, immediately before chilling, a considerably lower result may be obtained. This value is known as the lower or minimum pour point. If the sample is chilled through successive low temperature cycles

a value higher than the "maximum" pour point found by ASTM Method D97 is obtained. The ASTM has published a proposed method for "stable pour point" in which the oil is taken through three cycles ranging from +20 to −30°F.[4] The highest pour point found in any of the cycles is taken as the "stable pour point." This value may be as much as 40°F higher than the "maximum pour point" found by method D97. The "minimum" and "maximum" values obtained by method D97 may in turn differ by as much as 25°F.[13]

Pour Point Depressants. There are several methods by which the pour point of an oil can be reduced. If the pour point is of the "viscous" variety it can be reduced only by lowering the viscosity, either through removing some of the more viscous components or by adding a component of low viscosity. "Wax pour point" can be reduced either by removing some or all of the wax (dewaxing) or by adding a material which, through selective adsorption, alters the crystal structure of the wax in such a way as to enhance flow at low temperatures. Additives of this type are known as pour point depressants. Paraflow, which is a poly alkyl naphthalene made by condensing chlorinated wax with naphthalene in the presence of aluminum chloride, is probably the most widely known pour point depressant.[11, 29] Several others are available commercially Paraflow has very little if any effect upon the cloud point but may reduce the pour point by 50°F or more when used in concentrations of one to two per cent. Microscopic examination shows that this additive does not prevent the crystallization of wax but reduces the size of the crystals. It also reduces the amount of oil held, either by adsorption or entrainment, by the wax cyrstals. Both of these effects are probably caused by selective adsorption of the additive on the surface of the wax crystals during the initial stages of crystal formation, i.e., while the crystals are small.

The low temperature performance of an oil can be predicted only partially from its pour point, which is in essence the temperature below which the apparent viscosity becomes infinite at a very low rate of shear If an oil is chilled to a temperature below its pour point and then warmed, the lowest temperature at which it can be pumped, e g., to the bearings in an engine, is determined by the pour point[28] Such properties as cranking torque, on the other hand, which involve

high rates of shear in the oil, are related to the apparent viscosity at high shear-rate and not to the pour point.[28]

Viscosity Temperature Relationships

The viscosity temperature coefficient of all liquids is high and the temperature must be carefully defined in any expression of viscosity. The dependence of viscosity upon temperature has received much study. For lubricating oils the following empirical equation, often referred to as the Walther equation, serves adequately, at least over a considerable range:

$$\log \log (V + k) = A + B \log T, \tag{11}$$

where V is the kinematic viscosity in centistokes, T is the absolute temperature, A and B are constants for a given oil, and k is, except for very low values of V, a universal constant. A value of 0.8 was originally used for k, but the ASTM later found the equation to fit the experimental data better if a value of 0.6 is used for viscosities greater than 1 5 centistokes. This value is now used in charts published by the ASTM, and allowance has been made for the slight variation in k at low viscosity. The scales of ordinates and abscissae used in these charts are such that when viscosity is plotted against Fahrenheit temperature a straight line results. Charts are available for either kinematic or Saybolt viscosity. An ASTM chart, with several of the lines deleted, is shown in Figure 7, together with the viscosity temperature curves for some typical oils, both natural and synthetic * It will be observed that the viscosity temperature curve for the silicone is very flat, while that for the fluorocarbon is very steep. The slopes of the curves for petroleum oils are intermediate. Polyalkylene glycol has a slope intermediate between those of the silicone and the petroleum oils. The curve for the diester is roughly parallel to those for the mineral oils of 100 Viscosity Index. The slope of the curve for different mineral oils varies with composition. In general, paraffinic components contribute to a flat slope, while aromatic and naphthenic components contribute to a steep one. All the curves shown in Figure 7 are linear with the exception of one, (polyalkylene glycol), which shows a slight but distinct curvature throughout the temperature range. This curve is typical for this

* For a description of these synthetic oils see Chapter VIII.

class of oils. Curves drawn on this chart for petroleum oils are as a general rule linear down to the temperature at which a phase separation occurs, i.e., the cloud point. At temperatures below the cloud point, where the oil is not homogeneous but consists of a suspension of a solid phase in oil, the viscosity or apparent viscosity

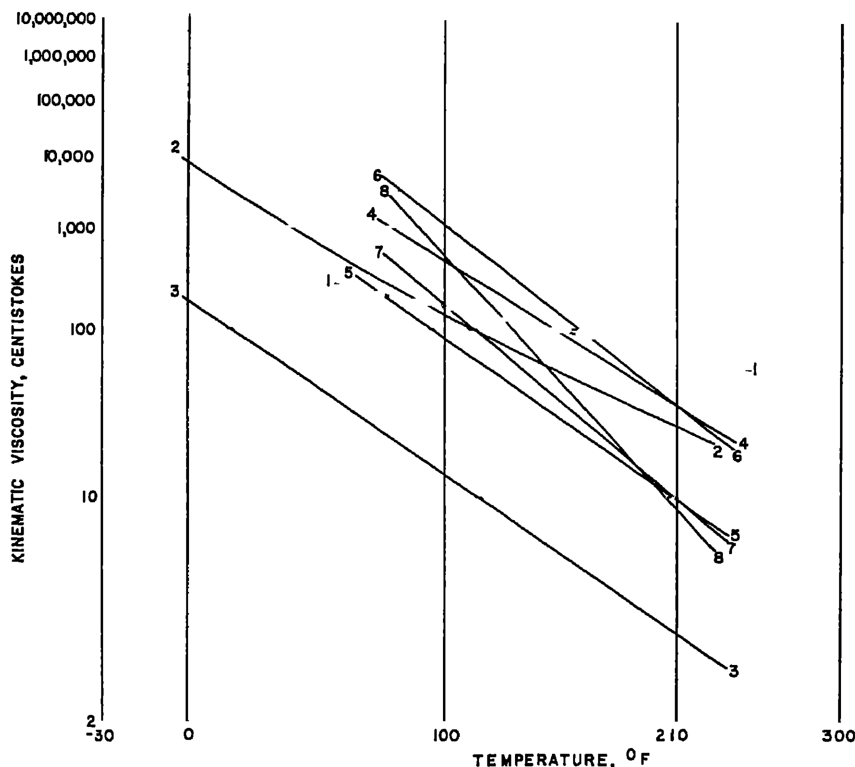


Figure 7. Viscosity-Temperature Curves for Typical Oils

1. Silicone
2. Polyalkylene glycol
3. Diester
4. Mineral oil, 100 VI
5. Mineral oil, 100 VI
6. Mineral oil, 0 VI
7. Mineral oil, 0 VI
8. Fluorocarbon

is higher than indicated by extrapolation of the linear portion of the viscosity-temperature curve. The magnitude of the deviation varies with the concentration of solid phase.

In the case of two component systems the function log log $(V + 0.6)$ of equation (11) is, for practical purposes, related linearly to

composition as well as to the logarithm of the absolute temperature. This makes it possible to calculate the viscosity of blends. A chart similar to the ASTM chart shown in Figure 7 but with a linear scale of abscissae is useful for determining the viscosity of blends graphically. Since the portion of the abscissa scale of the viscosity temperature chart ranging from 0 to 100°F is very nearly linear, it is often used for this purpose.

Many means have been suggested for expressing the variation of viscosity with temperature in terms of a single number. Only three of these will be discussed here, since none of the others has received general acceptance. The three which are most widely used are the slope of the ASTM curve, the Viscosity Index, and the Viscosity Pole Height.

Slope of ASTM Curve. A simple method of expressing change of viscosity with temperature is the slope of the curve on the ASTM chart. This may be determined graphically on the chart, or may be expressed mathematically. Walther suggested the B of equation (11) as a measure of slope. Bell and Sharp[8] proposed a slope number based on an ordinate scale, H, and an abscissa scale, K, in which:

$$H = 870 \log \log (V + k) + 154 \qquad (12)$$

and in which the K scale was chosen so that $K = 0$ at 210°F and $K = 1$ at 100°F. The slope then equals $\frac{H_2 - H_1}{K_2 - K_1}$. If the two temperatures chosen are 100 and 210°F, the equation reduces to:

$$\text{slope} = H_{100} - H_{210} \qquad (13)$$

The original tables of Bell and Sharp were based on equation (11) with a value of k of 0.8. Hirschler[22] has published a revised series of tables based on equation (11) with a value of k of 0.6. These tables give H values for viscosities ranging from 2 to 100,000 centistokes.

Slopes determined by the graphical method or by the method of Walther or Bell and Sharp are of course proportional, provided the same k value is used in the basic equation, since all three are based on equation (11). Of the three slope number scales, Hirschler's modification of the Bell and Sharp scale is preferred. It is more precise than the graphical solution and is more conveniently calculated than Walther's "B" value, since tables are available.

The slope number of petroleum lubricants varies from 200 for

paraffinic oils to 300 or more for those of naphthenic or aromatic nature. Slope number, like "H" values and the function log log $(V + 0.6)$, are additive. The slope numbers of a blend can therefore be calculated from the composition and the slope numbers of the components by simple arithmetic.

The use of slope numbers for characterizing lubricants has the disadvantage that oils of similar composition but different viscosity, e.g., light and heavy grades from the same crude source, usually have considerably different slope numbers.

Viscosity Index. The most commonly used method for expressing the relationship between viscosity and temperature is the Viscosity Index of Dean and Davis,[10, 13] which is based on an empirical scale. The standards are two series of lubricating oil fractions, the one obtained from a Pennsylvania crude which was arbitrarily assigned a Viscosity Index (VI) of 100 and the other from a Gulf Coast crude which was assigned a Viscosity Index of zero. VI is more nearly constant than slope number for oils of similar composition but different viscosity. The VI of an oil of a given viscosity at 210°F is calculated from its viscosity at 100°F and the viscosity at 100°F for each of the standards having a viscosity at 210°F equal to that of the unknown.

$$\mathrm{VI} = \frac{L - U}{L - H} \times 100 \qquad (14)$$

where L, H, and U are the viscosities at 100°F of the zero VI standard, the 100 VI standard, and the sample, respectively. Tables are available in the ASTM manual for determining Dean and Davis VI from either the kinematic or the Saybolt viscosity at 100°F and 210°F.

The Viscosity Index scale of Dean and Davis is in general use in the United States although it has the following deficiencies: (1) It is based on arbitrary standards. (2) It is not an additive property. (3) In the very high range of VI the scale becomes meaningless, since two oils of equal viscosity at 100°F but widely different viscosity at 210°F may have the same VI. For example an oil with a viscosity of 100 centistokes at 100°F and either 20 or 37 centistokes at 210°F has a VI of 150 on the Dean and Davis scale. (4) Anomalous VI's are obtained in the range of viscosities at 210°F below 8 centistokes.

Hardiman and Nissan[19] have revised the VI system to eliminate the last two of these deficiencies. They used viscosity data of Dean, Bauer, and Berglund[12] as a basis and showed that these data, which covered a range of viscosity from 8 to 40 centistokes at 210°F and VI's from 0 to 100, could be represented by the equation:

$$V_{100} = 2.714\ V_{210}^{n} \tag{15}$$

or

$$n = \frac{\log V_{100} - \log 2.714}{\log V_{210}} = \frac{\log V_{100} - 0.4336}{\log V_{210}} \tag{16}$$

They showed furthermore that VI is related to n by the empirical equation:

$$\text{VI} = 3.63\ (60 - \text{antilog}\ n) \tag{17}$$

It is possible, by means of equations (16) and (17), to calculate the Hardiman and Nissan Viscosity Index of an oil from its viscosities at 100°F and 210°F. Values obtained in this manner agree closely with Dean and Davis VI's in the range of 0 to 100, provided the viscosity at 210°F is greater than 8 centistokes. For higher Viscosity Indexes and for lower viscosities the Hardiman and Nissan Viscosity Index is free from the anomalies present in the Dean and Davis system.

Viscosity Pole Height. Next to the slope of the viscosity temperature curve on the ASTM chart and the Viscosity Index, the most widely used system for expressing viscosity-temperature relationships is the *Polhohe*, or Pole Height, of Ubbelohde.[28] This system is based on the premise, which is not strictly true, that viscosity-temperature curves on the ASTM chart for oils of different viscosity but from the same crude source or of a similar type intersect in a point. This point is known as the *Viscositätspol*, or Viscosity Pole. The vertical distance between the Viscosity Pole and a standard base line is the Pole Height. The Pole Height of paraffinic oils is of the order of 1 to 2, and of naphthenic oils 3 to 4 or higher.

Of the three systems discussed above, the slope of the ASTM curve is the most fundamental and the least arbitrary; however, the Viscosity Index is the most widely used. The reasons for the popularity of the latter system are threefold: (1) it was published first and was widely adopted at a time when no other system was

available, (2) it uses a convenient scale ranging from 0 to 100 for most commercial lubricants, and (3) VI shows little variation for different grades of oil of similar composition. The Pole Height offers little, if any advantage over either of the other two methods, and it is unlikely that it will supplant either of them. Of the various modifications of slope number and Viscosity Index, the Hirschler modification of the Bell and Sharp slope number and the Hardiman and Nissan modification of Viscosity Index probably have the most merit.

The slope number and Viscosity Index of a few typical oils, both natural and synthetic, are shown in Table 3. The oils represented

TABLE 3. VISCOSITY TEMPERATURE RELATIONSHIP FOR TYPICAL OILS

Oil	Kinematic Viscosity, Centistokes		Viscosity Index, Hardiman and Nissan Modification of Dean and Davis	Slope Number, Hirschler Modification of Bell and Sharp
	100°F	210°F		
Silicone[a]	160	65	182	73
Polyalkylene glycol[b]	135	21.9	152*	172*
Diester[c]	12.90	3.35	146	241
Pennsylvania type[d]	461.0	30	100.4	220
Pennsylvania type[d]	89.2	10	98.5	244
Gulf Coastal type[d]	1156.0	30	−1.0	272
Gulf Coastal type[d]	162.5	10	0.5	291
Fluorocarbon[e]	536	9.05	−690	386

[a] Data taken from circular on Dow Corning Fluids published by Dow Corning Corporation

[b] Data taken from reference 27, Chapter VIII

[c] Data taken from reference 13, Chapter VIII

[d] Data taken from reference 10, Chapter II

[e] Data taken from reference 28, Chapter VIII.

* These values do not have the same significance as the others, since the ASTM curve for this oil is not linear. However, the VI and slope number do indicate the average slope in the range of 100 to 210°F.

here are the same as those whose viscosity temperature curves are shown in Figure 7.

Viscosity Index Improvers. Certain high molecular weight polymers raise the Viscosity Index of an oil when added in relatively low concentration. The best known commercially used VI improvers include polybutene, polymethacrylate, and alklyated polystyrene.[26a] Their effect is partially one of normal blending. The polymers themselves possess relatively flat viscosity temperature curves, and their addition to a mineral oil raises the log log $(V + 0.6)$ at 210°F more than at 100°F. However, the better Viscosity Index improvers show effects too large to be accounted for on this basis alone.

The effectiveness of high molecular weight polymers in increasing the Viscosity Index of a mineral oil or other solvent is associated with the limited solubility of the polymer in the solvent. Evans and Young[16, 17] have proposed two theories to account for the influence upon Viscosity Index of polymers through their limited solubility. According to the first theory the polymer exists either in true solution or in colloidal suspension. For polymers of this nature the effect upon viscosity is known to be greater in the former state. If, therefore, the solubility is appreciably higher at 210°F than at 100°F, then the relative effect upon viscosity will be greater at the higher temperature and the Viscosity Index of the blend will be increased. The second theory is similar to the first except that it does not require a colloidal state but rather a highly convoluted state of the polymer molecules, caused by strong self-associating factors of the polymer in the poor solvent. A transition from true solution to the convoluted state, analogous to the change from solution to the colloidal state in the first theory, takes place with decreasing temperature. This effect is in certain cases so pronounced that the temperature viscosity coefficient over a narrow temperature range is positive, i.e., an increase in temperature results is an increase in viscosity. This point is illustrated in Table 4.

TABLE 4. VISCOSITY OF SOLUTION OF POLYBUTENE IN BENZENE[a]
Concentration, 10 g/liter

Temperature, °C	Viscosity, Centistokes
25 0	2.31
37 8	2 47
39 0	2 56
40 0	2 58
41 0	2 65
42.0	2 62

[a] Data from Evans and Young[17]

A similar theory has recently been advanced to account for the high Viscosity Index of silicones. Fox, Taylor, and Zisman[18] have concluded, on the basis of spreading pressure measurements, that silicone molecules are capable of coiling reversibly into helices made up of about six monomers per turn. They postulate that as the temperature is increased the polymer lengthens through uncoiling of the helix. They conclude further that this particular behavior, which is not found in the corresponding carbon derivatives, is associated with the large size of the silicon atom in comparison with that of the carbon atom.

Since the effectiveness of a polymer is dependent in a large degree upon its solubility characteristics and since solubility is determined both by the solute and the solvent, it follows that the relative effectiveness of a series of Viscosity Index improvers may be different for different oils. Evans and Young[17] determined the Viscosity Index of four different stocks, each with varying concentrations of three different VI improvers. The base stocks had Viscosity Index values of +105, −78, −190, and −324; the VI improvers were polybutene (I), a condensation product of highly chlorinated wax and naphthalene (II), and polycetyl methacrylate (III). The 105 VI oil rated the three polymers in the order III, II, I, with III the most effective. The −78 VI oil rated them in the order II, III, I and the −324 VI oil in the order I, II, III The −190 oil rated II above III and I either best, intermediate, or poorest, depending upon the concentration range.

The ASTM viscosity temperature curves for oils containing Viscosity Index improvers are as a general rule not linear, although they may approach linearity. The exact behavior of such oils over a wide temperature range can be determined only from viscosity measurements at additional temperatures.

When oils containing VI improvers are subjected to high rates of shear they often suffer a loss in viscosity and Viscosity Index.[17a, 18a, 23a] This loss in viscosity may be either or both of two fundamentally different types, namely, permanent and temporary. The former is believed to be associated with a breakdown, either mechanical or chemical, of the relatively large polymer molecules into smaller units. The latter, which is simply a departure from Newtonian behavior, is believed to be caused by an alignment of the polymer molecules at high rates of shear.

Polymers differ in their viscosity stability, both permanent and temporary. In general, those of high molecular weight, which are incidentally the most effective as VI improvers, are the most susceptible to permanent loss in viscosity at high shear rates.[26a] The choice of a VI improver for a given application is, therefore, often a compromise between optimum effectiveness and viscosity stability Fleming and coworkers[17a] ran tests of moderate severity in passenger car engines on five crankcase oils composed of various combinations of three base stocks and three VI improvers. They found permanent

losses in viscosity at 210°F ranging from 0.8 to 4.5 Saybolt units, and losses in Viscosity Index ranging from 3 to 9 units.

Fleming and coworkers[17a] measured apparent viscosity at 210°F as a function of rate of shear and found that a polymer blend exhibited only a 6 per cent temporary loss in viscosity at shear rates of 500,000 to 700,000 reciprocal seconds. Georgi,[18a] on the other hand, ran similar tests on three blends, each containing a different VI improver, and found in every case that the apparent viscosity of the blend approached the viscosity of the undoped oil at shear rates of only 140,000 reciprocal seconds.

Viscosity Pressure Relationships

The viscosity of a liquid is a function of both temperature and pressure. A small increment in pressure has a much smaller effect than a small increase in temperature. Considerably less work has therefore been done on the effect of pressure. However, lubricating oils may be subjected to extremely high pressures, under which their viscosities are increased appreciably.

Much of the influence of either pressure or temperature is undoubtedly connected with the effect of these variables upon intermolecular distances A decrease in temperature or an increase in pressure decreases the distance between molecules. This decrease is evidenced by an increase in density. Faust proposed the theory that the viscosity of a liquid at varying temperature and pressure is a function of density alone.[20] However Bridgeman showed, by measurement on forty-three liquids at two temperatures (30° and 75°C) and several pressures ranging from 1 to 12,000 atmospheres, that Faust's theory is an oversimplification.[20] When viscosity is plotted against density for two temperatures, two curves are obtained, one for each temperature.

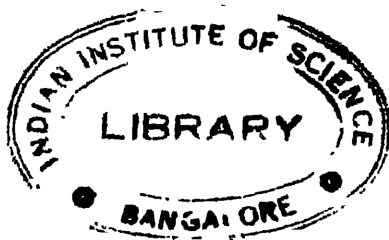
Most of the work reported in the literature on the effect of pressure upon the viscosity of lubricating oils was done by Dow and coworkers.[14, 15, 26] They measured the viscosities of a number of lubricating oils at 100, 130 and 210°F and at pressures ranging from 1 to 4000 atmospheres. The effect of composition upon the slope of the viscosity-pressure curve was found to be analogous to the effect upon the viscosity-temperature curve, viz , paraffinic oils show the least effect and aromatic and naphthenic oils show a greater effect.

This point was established by measurements on a Pennsylvania oil, which is highly paraffinic; an Oklahoma oil, which is somewhat less paraffinic; and a California oil, which contains a low concentration of paraffinic components. The Pennsylvania oil with a viscosity of 40 centipoises, showed a 25-fold increase in viscosity at a pressure of 26,000 psi. The Oklahoma and a California sample of the same viscosity at 130°F and atmospheric pressure showed a 35- and 100-fold increase, respectively, at 26,000 psi.[14] Additional measurements on the acetone raffinate and extract of a Pennsylvania Neutral[26] and on Russian and Rumanian[15] oils confirmed the earlier observation by Dow that mineral oils of low viscosity-temperature slope (high Viscosity Index) have low viscosity-pressure slopes.

Bibliography

1. Amner, J. W., and Blott, J F. T., "The Principles of Rheological Measurement· Report of the Second Conference of the British Rheologists Club," London, Thomas Nelson and Sons, Ltd., 1949.
2. Arveson, M. H., *Ind. Eng. Chem.*, **24**, 71–5 (1932).
3. Arveson, M. H., *Ind. Eng. Chem.*, **26**, 628–34 (1934).
4. "A.S T.M. Standards on Petroleum Products and Lubricants," pp. 10–19, Philadelphia, A.S.T.M. Committee D-2, 1945.
5. *Ibid* , pp. 67–70, 1947.
6. Beerbower, A., Sproule, L. W., Patberg, J B., and Zimmer, J. C., *Inst. Spokesman*, **6**, No. 8, 4–7, No. 9, 1–7 (1942); No 10, 6–7, No. 11, 4–6 (1943).
7. Barnard, D. P., "Science of Petroleum," Vol II, pp. 1071–9, Oxford University Press, 1938.
8. Bell, T. G., and Sharp, D. H., *Oil Gas J.*, **32**, 13–16 (1933).
9. Blott, J. F T., and Samuel, D. L., *Ind. Eng. Chem.*, **32**, 68–72 (1940).
10. Davis, G. H. B , Lapeyrouse, M., and Dean, E W., *Oil Gas J.*, **30**, 92 (1932).
11. Davis, G. H. B., and Zimmer, J. C., "Science of Petroleum," Vol IV, pp 2673–8, Oxford University Press, 1938.
12. Dean, E. W., Bauer, A D., and Berglund, J. H., *Ind. Eng. Chem.*, **32**, 102–7 (1940).
13. Dean, E. W , and Davis, G. H. B , *Chem & Met. Eng* , **36**, 618–9 (1929).
14. Dow, R. B., *J. Applied Phys.*, **8**, 367–72 (1937)
15. Dow, R. B., McCartney, J. S., and Fink, C E , *J. Inst. Petroleum*, **27**, 301–9 (1941).
16. Evans, H. C., and Young, D. W., *Ind. Eng. Chem.*, **34**, 461–6 (1942).
17. Evans, H. C., and Young, D. W., *Ind. Eng. Chem.*, **39**, 1676–81 (1947).
17a. Fleming, C L., Geddes, B. W., Hakala, N. V , and Weisel, C A , *S.A.E. Quart. Trans.*, **4**, 410–7 (1950).
18 Fox, H. W., Taylor, Paula W., and Zisman, W. A , *Ind. Eng Chem* , **39**, 1401–9 (1947).
18a Georgi, C. W., *S.A.E. Quart. Trans* , **3**, 431–40 (1949).
19. Hardiman, E W., and Nissan, A. H., *Inst Petroleum*, **31**, 255–70 (1945)
20. Hatschek, E., "The Viscosity of Liquids", Chapter VI, London, G Bell and Sons, Ltd., 1928.

21. Hennenhofer, J., *Oel u. Kohle*, **39**, 679–85 (1943); *Chem. Abstracts*, **38**, 1346 (1944)
22. Hirschler, A. E., *J Inst. Petroleum*, **32**, 133–61 (1946).
23. Kurtz, S S., *Ind. Eng. Chem* , **34**, 770 (1942).
23a. Needs, S. J., paper presented at API meeting, Chicago, Nov. 7, 1949.
24. *Proc. Am. Soc. Testing Materials*, **31**, Part I, 469 (1931)
25. "S.A.E. Handbook", New York, Society of Automotive Engineers, 1947
26. Thomas, B. W., Ham, W. R., and Dow, R. B., *Ind. Eng. Chem.*, **31**, 1267–70 (1939).
26a. Van Horne, W. L., *Ind. Eng Chem.*, **41**, 952–9 (1949).
27 Velikovskii, D. S., *Petroleum*, **11**, 105–12 (1948).
28. Wilkin, R. E., Oak, P T., and Barnard, D. P., *S A E. Journal*, **22**, 213–20 (1928)
29. Zimmer, J. C., Davis, G. H. B , and Frolich, P K., *Penna. State Coll. Min. Ind. Expt. Sta. Bull.*, **12**, 57–63 (1933).



Chapter III*

OXIDATION

Introduction

While oils for various applications must meet widely different specifications, they have one requirement in common—they should undergo a minimum of change during use. Changes in properties during operation are due partly to extraneous contamination, but largely to chemical changes in the oil molecules themselves. These chemical reactions are principally those involving oxidation.

Oxidation of a lubricant in some cases benefits certain properties. For example King[25] found, in a test employing a journal bearing at a pressure of 1000 lb per square inch of projected area, that pre-oxidation of a mineral oil reduced its coefficient of friction and increased its "critical seizure temperature" by 145°C. Similar results were published by Exline, Kramer, and Bowman.[17] However, the same effect could probably have been realized by the addition of a small amount of polar compound, without the attendant disadvantages of the oxidation treatment. Another example is cited by Baker,[1] who reports that the addition of 10 per cent of used turbine oil to a fresh charge imparts rust-preventive properties not present in the fresh oil. This method of rust prevention is not without penalty, however, since other properties of the oil, notably service life and the ability to separate entrained moisture, are drastically damaged. It has accordingly been largely supplanted by the incorporation of a trace of highly effective compound. These additive-type oils are much more effective as rust preventives than the previous blends of new and oxidized oil, and the additive has very little effect upon other properties.

Oxidation of a lubricating oil leads to such difficulties as bearing corrosion, ring sticking, lacquer and sludge formation, and excessive viscosity. It is sometimes possible to overcome the harmful effect of a given class of oxidation products. An example of this approach to the problem is the addition of dispersants, which peptize colloidal oxidation products and prevent their deposition as lacquer.† An-

* This chapter, which is based on a paper originally published in *Chemical Reviews*, **38**, 197–226 (1946), is used with the permission of The Williams and Wilkins Company, publishers of *Chemical Reviews*.

† See Chapter V

other example is the use of certain sulfur-containing additives which, in addition to performing other functions, passivate bearing surfaces and thus prevent corrosive acids which may be present in the oil from attacking the bearings.* While methods such as these are commonly used, the over-all control of oxidation is nevertheless essential, not so much to eliminate the need for specific additives other than antioxidants, but to reduce the burden imposed upon them.

Oxidation Products

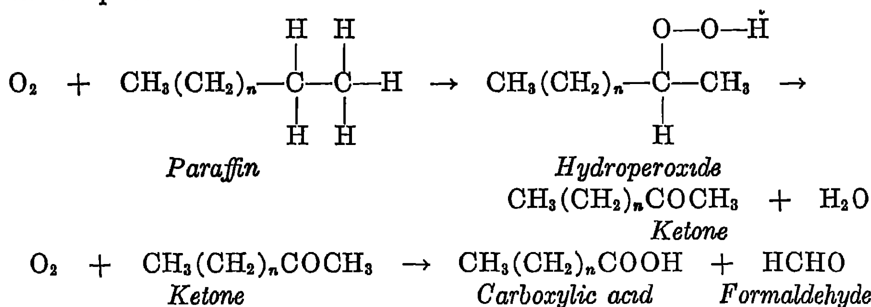
Pure Hydrocarbons. Lubricating oils are composed of such a complex mixture of hydrocarbons that it is extremely difficult to identify specific compounds in their oxidation products, except for such degradation products as water, carbon dioxide, and some of the lower carboxylic acids. However, since lubricating oils are composed primarily of hydrocarbons, including three main groups—namely, paraffin, naphthene, and aromatic—it is of interest to examine the literature on the oxidation of pure hydrocarbons of these three types under conditions comparable to those encountered by oils in actual use.

Chavanne and coworkers[4,5,16] have studied the oxidation of a few paraffins and naphthenes. They oxidized *n*-decane, *n*-nonane, and *n*-octane with oxygen at atmospheric pressure and a temperature of 120°C. The gaseous oxidation products, which account for 10 per cent or so of the total, were similar in all three cases, and included 30 to 40 per cent of carbon dioxide, 1 to 3 per cent of carbon monoxide, 5 to 7 per cent hydrogen, and 1 to 2 per cent of saturated hydrocarbons. The liquid products contained water, succinic acid, and formaldehyde. The three hydrocarbons produced a preponderant amount of methyl octyl, methyl heptyl, and methyl hexyl ketones, respectively, as well as a series of carboxylic acids ranging from formic to C_{n-1}, where n is the number of carbon atoms in the hydrocarbon. *n*-Octane formed, in addition, a small amount of octanol. These data would indicate that attack of a paraffin by oxygen under these conditions is not at the terminal carbon, but at the carbon in the CH_2 group adjacent to the terminal CH_3 group. This is consistent with the views of Burwell,[3] who states that whereas at high temperatures terminal carbons are attacked to produce

* See Chapter IV

aldehydes, at lower temperatures (*ca.* 150°C) the beta carbon is involved primarily, the gamma secondarily, and so on toward the center of the molecule. Thus formic, acetic, and propionic acids would be expected in order of decreasing concentration. Fenske *et al.*[18, 19] actually found this to be the case in an analysis of the volatile products resulting from the oxidation of a lubricating oil at temperatures of 130 to 180°C.

George, Rideal, and Robertson[20] found that C_{15} and C_{25} paraffins and alkylbenzenes are oxidized at 100 to 120°C to form hydroperoxides, which accounted for 60 to 80 per cent of the oxygen absorbed by the alkylbenzenes, and which decomposed almost exclusively to give ketones in the case of the paraffins. The presence of peroxides in high concentration in the early stages of oxidation has also been shown by Larsen and coworkers.[27] For example, in the oxidation of decalin at 110°C, peroxide is the principal oxidation product until upwards of 5000 cc of oxygen per 100 g of hydrocarbon has been absorbed. Balsbaugh and Oncley[2] found that tetralin, decalin, and cetane are oxidized almost exclusively to peroxides in the early stages of the reaction at temperatures ranging from 30 to 100°C. Similar results have been reported by Dornte[13] and by Denison[12] regarding the oxidation of white oils. Several investigators have shown that water is one of the principal oxidation products of lubricating oils.[13, 18, 27, 28] Fenske and coworkers[18] report that water can account for as much as 44 to 70 per cent of the oxygen absorbed by an oil. In view of the above, the mechanism of the oxidation of a paraffin at temperatures in the range of 100 to 200°C. can be postulated as follows:



$$O_2 + CH_3(CH_2)_n{-}CH_2{-}CH_3 \rightarrow CH_3(CH_2)_n{-}CH(OOH){-}CH_3 \rightarrow$$

Paraffin *Hydroperoxide*

$$CH_3(CH_2)_nCOCH_3 + H_2O$$

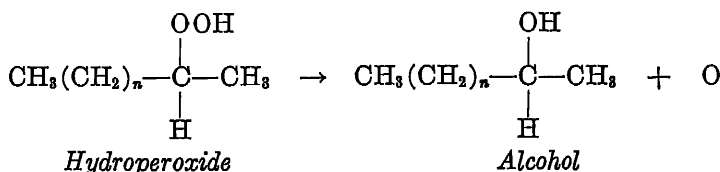
Ketone

$$O_2 + CH_3(CH_2)_nCOCH_3 \rightarrow CH_3(CH_2)_nCOOH + HCHO$$

Ketone *Carboxylic acid* *Formaldehyde*

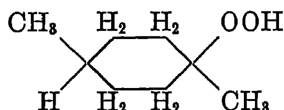
In addition, there would be some primary attack on the gamma rather than the beta carbon atom. This would result in the formation of a ketone of the same number of carbon atoms, but with the C=O group shifted one carbon atom toward the center of the molecule.

The corresponding carboxylic acid would contain one less carbon atom than shown above, and acetaldehyde, rather than formaldehyde, would be split off The acids can be oxidized further through attack at other carbon atoms, and the aldehydes are probably oxidized further to the corresponding carboxylic acids and, to some extent, to carbon dioxide and water. The formation of alcohols would require a reducing action on a hydroperoxide, the latter losing one atom of oxygen in acting as an oxidizing agent. Esters could be formed by the condensation of an acid and an alcohol.



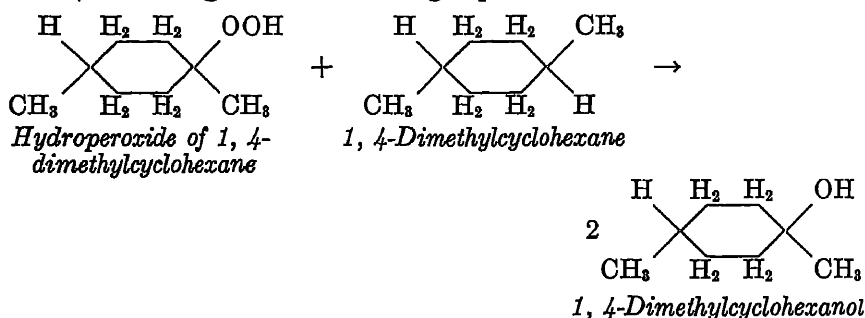
Chavanne and Bode[4] have made an extensive study of the oxidation products of 1,4-dimethylcyclohexane. Conditions were the same as in the case of the oxidation of the three paraffins mentioned above, except that the temperature was 100°C instead of 120°C. They started with 116 g of hydrocarbon and recovered 21 g of unreacted material, so that 95 g was oxidized. The oxygen consumed amounted to 30.7 g, and 123 g of oxidation products were recovered, as compared with a theoretical value of 95 + 30.7, or 125.7 g. The principal oxidation product was 1,4-dimethylcyclohexanol, which was present in sufficient quantity so that 30 g were recovered in pure form. Other products included water (amount not given), carbon dioxide (5.2 g), β-methyl-δ-acetylvaleric acid (8–9 g), acetic acid (4–5 g), β-methylvaleric acid (2–3 g), dimethylcyclohexanediol (5.5 g), and acetonylacetone (0.5 g). Small amounts of hydrogen, carbon monoxide, methane, ethane, and formic acid were also detected.

The authors postulated the formation of a hydroperoxide,



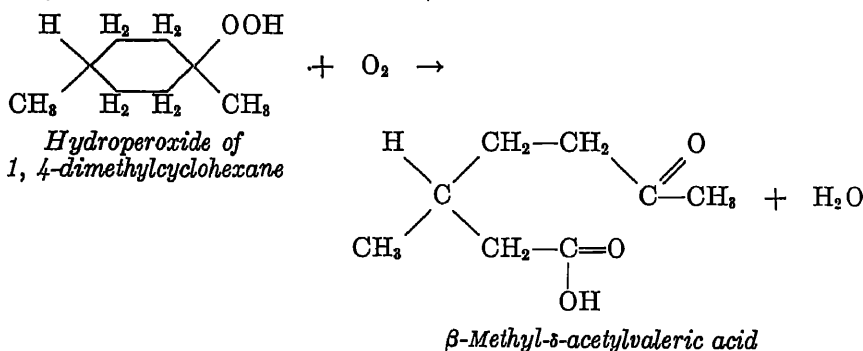
as the first step in the oxidation of 1,4-dimethylcyclohexane In that respect, the mechanism would be identical with that proposed earlier in the chapter for the oxidation of a paraffin, except that a tertiary rather than a secondary carbon atom is the vulnerable point of the molecule. The next step differs somewhat, however. The

paraffin peroxide apparently decomposes largely through dehydration to give the corresponding ketone and, to a lesser extent, by reduction to the alcohol. The naphthene peroxide, on the other hand, apparently decomposes largely through reduction to the alcohol. This may be due in part to the fact that the tertiary carbon atoms in this particular hydrocarbon act as reducing agents for the peroxide, according to the following equation:



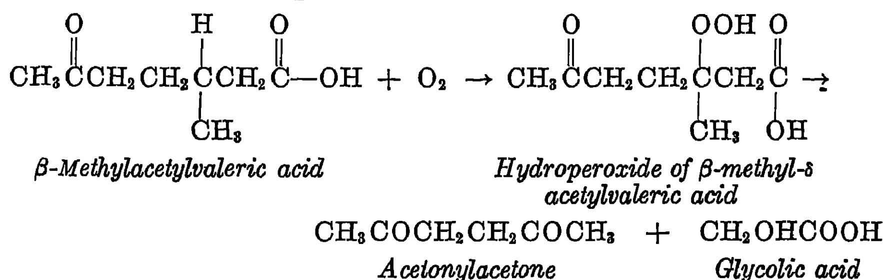
Hydroperoxide of 1, 4-dimethylcyclohexane *1, 4-Dimethylcyclohexane* *1, 4-Dimethylcyclohexanol*

The formation of the diol can be explained in the same manner. The other oxidation products no doubt form as a result of further oxidation of the hydroperoxide, resulting in rupture of the naphthene ring. This mechanism necessarily differs from that involved in the paraffin in that a ketone cannot be formed, except by rupture of a C—C bond, for a tertiary carbon atom is involved. Thus the peroxide itself, and not the ketone, is oxidized further. Another difference is to be found in the oxidation products. The paraffin oxidizes to give first a peroxide, then a ketone, then an acid plus a "volatile oxidation product"—namely, formaldehyde or acetaldehyde or the corresponding acid. The naphthene peroxide can be oxidized with a rupture of a C—C bond and still form a product containing the original number of carbon atoms, as follows:



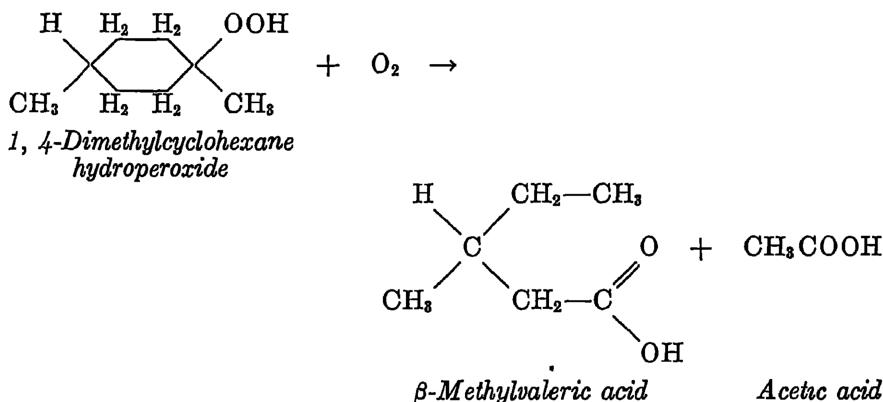
Hydroperoxide of 1, 4-dimethylcyclohexane *β-Methyl-δ-acetylvaleric acid*

Further attack of this molecule at the other tertiary carbon atom would explain the observed formation of acetonylacetone, as indicated by the following mechanism:



β-Methylacetylvaleric acid *Hydroperoxide of β-methyl-δ acetylvaleric acid*

Glycolic acid was not reported by the authors. It may have been present and escaped detection, or it may have oxidized further to simpler end products like formic acid and carbon dioxide and water. The formation of β-methylvaleric acid can be explained by the further oxidation of the hydroperoxide of the hydrocarbon with two molecules of oxygen, and a split of the naphthene ring on either side of the tertiary carbon. This would result in the formation of one molecule of acetic acid and one of β-methylvaleric acid.

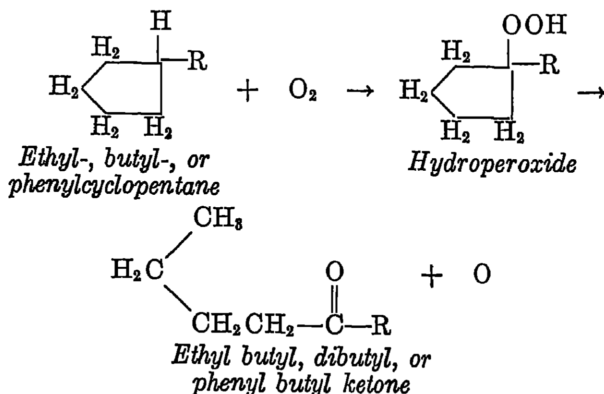


1, 4-Dimethylcyclohexane hydroperoxide *β-Methylvaleric acid* *Acetic acid*

This does not explain the formation of hydrogen, methane, and ethane, which are probably formed through cracking. However, since these substances are formed only in very low concentration in comparison with the other products, their presence does not invalidate the reaction mechanisms as outlined above.

Dupont and Chavanne[16] studied the oxidation of the three cyclopentane derivatives ethyl-, butyl-, and phenylcyclopentane, again under conditions of slow oxidation. In

straight-chain ketone containing the original number of carbon atoms. These were ethyl *n*-butyl ketone, an unidentified nine-carbon ketone which we shall assume to be dibutyl ketone, and phenyl butyl ketone, respectively. These three naphthenes probably formed hydroperoxides at the tertiary carbon atom in the same way that dimethylcyclohexane was oxidized; however, the peroxide then decomposed principally by reduction to the aliphatic ketone rather than to the cyclic alcohol as in the case of the cyclohexane derivative.

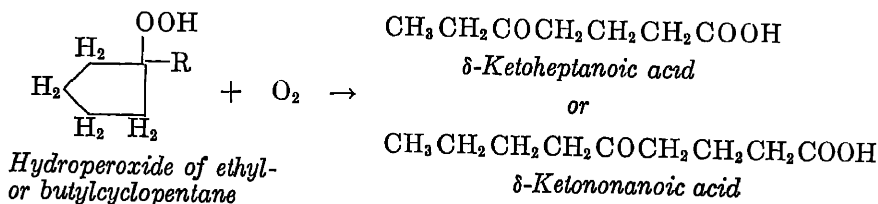


Ethyl-, butyl-, or phenylcyclopentane *Hydroperoxide*

Ethyl butyl, dibutyl, or phenyl butyl ketone

Thus the end product resembles that formed from a paraffin, the only difference being that the paraffin hydroperoxide decomposes to the ketone by dehydration, losing one molecule of water, while the naphthene does so by reduction, losing one atom of active oxygen. The reason for the difference in the behavior of the C_5 and C_6 naphthenes is not clear. It could have been caused by the presence of two tertiary groups in the latter and only one in the former, or by the difference in size of either the ring or the side chains, or possibly to a difference in conditions.

Ethyl- and butylcyclopentanes also formed the δ-keto derivatives of heptanoic and nonanoic acids, respectively. These were probably formed by oxidation of the peroxide in the same manner in which β-methyl-δ-acetylvaleric acid was produced from dimethylcyclohexane.

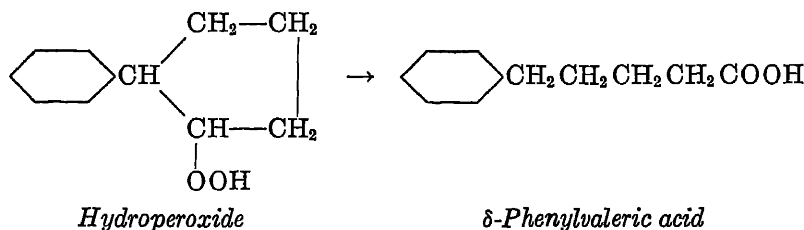


Hydroperoxide of ethyl- or butylcyclopentane

δ-Ketoheptanoic acid

δ-Ketononanoic acid

The former cyclopentane derivative also produced formic and propionic acids, and the latter butyric and valeric acids as products of further oxidation. Phenylcyclopentane also produced δ-phenylvaleric acid and benzyl alcohol. The formation of the former is of particular interest. This compound has the same empirical formula as the hydroperoxide of phenylcyclopentane; hence the acid could conceivably be formed from the peroxide by a molecular rearrangement. The peroxide in this case would probably not be the one with oxygen attached to the tertiary atom, but the one with oxygen attached to the naphthene carbon adjacent to it. The rearrangement would then include a break of a C—C bond, the transfer of a hydrogen atom from one carbon to another, and the transfer of an OH group from oxygen to carbon. Benzyl alcohol is possibly a degradation product of this acid.



Hydroperoxide *δ-Phenylvaleric acid*

Stevens[37] and Stevens and Roduta[38] have made an interesting study of the slow oxidation of a series of benzene derivatives. They bubbled oxygen through the hydrocarbon for a number of days at temperatures ranging from 80 to 140°C and analyzed the products formed. Their data are summarized in Table 5. It will be seen that oxidation always centers about a carbon atom attached to the benzene ring. The methylbenzenes all formed aldehydes containing the same number of carbon atoms as the parent molecule, and the substituted benzenes containing larger groups all formed ketones containing a phenyl group plus the other R group originally attached to the benzene ring, or the smaller of the two groups in the case where two groups were present. Acids, resulting from the further oxidation of aldehydes or ketones, were also formed, as well as acids of low molecular weight which formed from the fragments split off in the formation of ketones from secondary compounds. Alcohols were not formed in detectable quantity in any instance

While Stevens does not report the presence of peroxides, it would

appear probable that oxidation in every case was initiated by peroxidation to the hydroperoxide at the carbon adjacent to the benzene ring. This peroxide then decomposes by dehydration to the aldehyde or ketone, respectively, depending upon whether the starting material contained methyl or larger groups, or by the loss of a molecule of alcohol to form a ketone in the case of a tertiary hydrocarbon. The

TABLE 5. OXIDATION OF BENZENE AROMATICS
Data from Stevens[37] and Stevens and Roduta[38]

	Oxidation Temperature, °C	Conditions (Time, hr)	Grams of Product per 100 g of Hydrocarbon
Toluene	100	48	Trace of aldehyde
m-Xylene	100	30	2 1 g toluic aldehyde; 1.1 g toluic acid
Mesitylene (1,3,5-trimethylbenzene)	100	24	2 1 g 1,3-dimethylbenzaldehyde, 1.4 g mesitylenic acid
Durene (1,2,4,5-tetramethylbenzene)	100	9	5.8 g durylic aldehyde; 4 9 g durylic acid
p-Cymene (1-methyl-4-isopropylbenzene)	85	14	1.2 g cumic aldehyde; 0 8 g cumic acid
	102–4	14	Cumic aldehyde; cumic acid; 2 g *p*-tolyl methyl ketone; formic acid
Ethylbenzene	110–15	24	19 g acetophenone
n-Propylbenzene	102–4	25	Resin
	78	36	Trace of propiophenone
Cumene (isopropylbenzene)	102–4	23	4 g acetophenone
	80	32	Formic acid
tert-Butylbenzene	102–4	25	Trace of nonvolatile residue
Ethylmethylphenylmethane	119	14–29	2–10 g acetophenone
	140	90	7.5 g acetophenone, 4 2 g benzoic acid
n-Butylmethylphenylmethane	119	14–29	2–10 g acetophenone, butyric acid identified by odor
Methyldiphenylmethane	119	14–29	2–10 g benzophenone, formic acid
Triphenylmethane	119	14–29	2–10 g benzophenone; phenol
Diphenylmethane	119	14–29	2–10 g benzophenone

aldehydes may then be further oxidized to acids, and the alcohols to aldehydes and then to acids. The ketones are oxidized further to benzoic acid, probably by the same mechanism proposed earlier for the oxidation of a paraffin to the acid of lower number of carbon atoms via the hydroperoxide and ketone. These reactions, which would explain all of the products Stevens reports, are illustrated below;

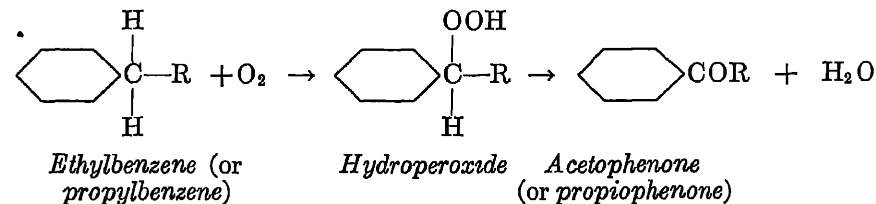
Durene (ring with four CH_3 groups) + O_2 → Hydroperoxide (ring with three CH_3 groups and $C(H)(H)OOH$) → Durylic aldehyde (ring with three CH_3 groups and CHO) + H_2O

Durene *Hydroperoxide* *Durylic aldehyde*

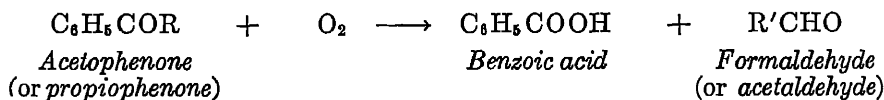
Durylic aldehyde (ring with three CH_3 groups and CHO) + $1/2\ O_2$ ⟶ Durylic acid (ring with three CH_3 groups and $COOH$)

Durylic aldehyde *Durylic acid*

The reactions of toluene, xylene, mesitylene, and *p*-cymene may be written in exactly the same manner, the products in every case being aldehydes and acids containing the same structure in the carbon skeleton as the original hydrocarbon. The reaction for ethylbenzene (and *n*-propylbenzene) is represented as follows:

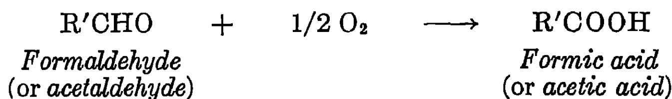


Ethylbenzene (or *propylbenzene*) *Hydroperoxide* *Acetophenone* (or *propiophenone*)



$$C_6H_5COR + O_2 \longrightarrow C_6H_5COOH + R'CHO$$

Acetophenone (or *propiophenone*) *Benzoic acid* *Formaldehyde* (or *acetaldehyde*)

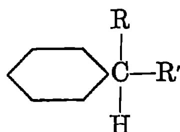


$$R'CHO + 1/2\ O_2 \longrightarrow R'COOH$$

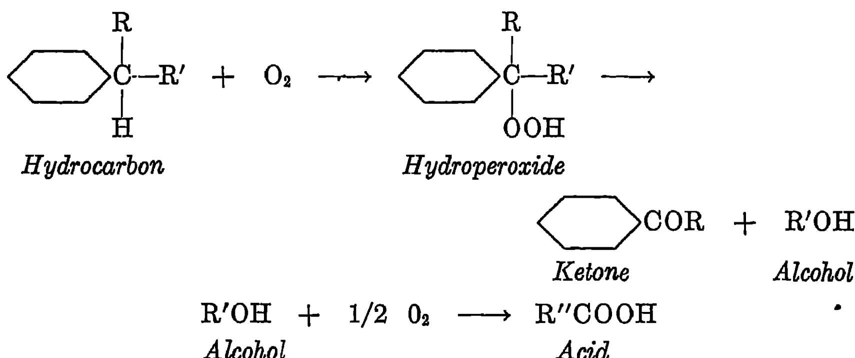
Formaldehyde (or *acetaldehyde*) *Formic acid* (or *acetic acid*)

Benzophenone could be formed from diphenylmethane by the same mechanism shown for the oxidation of ethylbenzene to acetophenone.

Cumene, ethylmethylphenylmethane, methylphenylpropylmethane, butylmethylphenylmethane, methyldiphenylmethane, and triphenylmethane can all be represented by the structural formula,



where R and R′ are H or alkyl or phenyl groups which may be alike or different. R is the smaller of the two in cases of unequal size. *p*-Cymene may also be thought of as belonging to this group, although it contains an additional methyl group on the benzene ring. These hydrocarbons are probably oxidized according to the following scheme:



tert-Butylbenzene cannot form a hydroperoxide at the carbon adjacent to the benzene ring, since this is a quaternary carbon. This may account for the fact that very little oxidation of this compound took place under conditions comparable to those for the other hydrocarbons.

Chernozhukov and Krein[7] studied the oxidation products of a number of hydrocarbons, although they did not report the oxidation products in detail as did the previously reported investigators. Their technique differed somewhat in that they used a bomb, and oxygen or air at a pressure of 15 atm. They used temperatures of 110 to 150°C for the most part, which are comparable to those used by Chavanne

and by Stevens. They found that substituted naphthenes are more unstable than unsubstituted ones, and attribute this to oxidation at the carbon of the ring attached to the alkyl group. They point out that this behavior—namely, the splitting of the ring—is in marked contrast to that of aromatic rings, which remain intact. Both of these observations are in line with the mechanisms proposed above for the initial oxidation of naphthenes and aromatics. They found that aromatics in general tend to give condensation products to a much greater extent than do naphthenes.

Larsen, Thorpe, and Armfield[28] studied the rate of oxygen absorption of a number of hydrocarbons at temperatures of 110 to 150°C and at an oxygen pressure of 1 atm. While they did not analyze the products for specific compounds, they did report various

TABLE 6. OXIDATION PRODUCTS OF FIVE CLASSES OF HYDROCARBONS
Data taken from Larsen, Thorpe, and Armfield[28]; all values expressed as percentage of total oxygen consumed

Class of Hydrocarbon	Free Acid	Combined Acid (Ester)	Peroxide	Alcohol and Phenol	Carbonyl	H_2O	CO_2	Volatile Acids
Paraffin	14 3	16 3	4 1	1 9	46 0	43 9	4 7	—
Naphthene and alkylnaphthene	11 2	17 0	13.5	8 9	51 4	21 9	3.8	0 6
Aromatic naphthene	6 1	23 1	4 3	8 5	27.2	16 7	1.2	0 4
Alkylbenzene	9 5	12 7	6 7	3.3	36 3	18 2	6 5	Trace
Naphthalene and alkylnaphthalene	6 9	16 3	1.4	9 4	9 6	51.3	7 8	1 6

functional groups. Thirty-nine compounds were investigated. These are tabulated in the section on "Oxidation Rates." The average values for the products of oxidation of five classes of compounds are given in Table 6. Conditions of oxidation were 1 atm of oxygen and 110°C, except in the case of the less reactive naphthalene compounds, in which case the temperature was raised to 150°C. The total amount of oxygen absorbed varied from less than 100 cc to more than 10,000 cc per mole. In most cases it was of the order of 5000 cc per mole

The figures in Table 6 cannot be regarded as absolute, since the total of the various products for a given hydrocarbon varied from 53 to 157 per cent of the total oxygen absorbed However, in most cases these totals lay between the limits of 80 to 120 per cent, and

the data shown in Table 6 are probably quite accurate as regards the average distribution of oxygen. Peroxides do not constitute a major oxidation product; however, Larsen *et al.* have shown[27] that peroxide content rises sharply in the early stages of oxidation and then falls. The free acid, alcohol, carbonyl, water, and volatile acid can all be explained as decomposition products, and further oxidation products of the peroxides and the combined acids, as determined by saponification value, by condensation reactions.

No value is listed for the average value under "volatile acids" for paraffins, since this value was reported for only one paraffin, hydropolyisobutylene. The value of 6.0 per cent reported is considered significant, in view of the fact that it is so much higher than those for the other hydrocarbons. It will be recalled that earlier in the chapter it was pointed out that, according to the proposed theory, a paraffin can be oxidized to an acid only through the splitting off of a C_1, or sometimes C_2, or larger, fragment, which would appear as aldehyde or acid. Polyisobutylene also showed a relatively high percentage of oxygen absorbed as "volatile acid" (6.3 per cent), although the other olefin examined, tetraisobutylene, gave only 0.8 per cent.

Larsen *et al.*[27] found, as did Chernozhukov and Krein, that aromatics give condensation products which darken the oil and precipitate, whereas paraffins and naphthenes remain homogeneous and light in color upon oxidation.

Mixtures and Petroleum Fractions. Larsen *et al.*[27] also determined functional groups in the oxidation products of a number of lubricating oils. Oxidation was carried out in the same equipment and under the same conditions used in the study of pure hydrocarbons, namely, 1 atm of oxygen and 110 or 150°C. The results for nine oils are shown in Table 7. The first seven are lubricating oil fractions, while the eighth is a synthetic oil made by polymerization of cracked-wax olefins. The last is a white oil. Both of the last two are aromatic-free. The first six are California furfural raffinates of various stages of extraction, as indicated by the progressively increasing Viscosity Index. It will be observed that as aromatics are removed there is a marked tendency toward a lower asphaltene content in the oxidized oil. This is of course one of the main purposes of solvent extraction, and is consistent with the conclusion based upon work on pure hydrocarbons that aromatics give dark insoluble condensation products.

Extraction also results in a higher conversion of oxygen to water, and slightly less to carbon dioxide and to volatile acids. No trends are apparent in the free or combined acids, nor in the alcohols and carbonyl. No peroxides were found in the oxidation products of the California oils, indicating that any peroxides formed were unstable under these conditions, and immediately reacted further. The two aromatic-free oils formed no asphaltenes, and formed less carbon dioxide and water and more intermediate oxidation products. This was particularly true at the lower temperature. Comparison of results on the synthetic oil at the two temperatures shows that the higher temperature favors the decomposition of peroxides and carbonyl, and the formation of carbon dioxide and water.

A comparison of the data on the lubricating oils as a whole with Table 6 reveals that the former correspond most closely to the alkylnaphthalenes in their oxidation products. This would indicate that this class of compounds may be the "front line" which bears the brunt of the attack of a lubricating oil by oxygen. This phase of the subject will be discussed in greater detail in a later section.

Dornte and coworkers[13, 14, 15] studied the oxygen absorption of a number of oils, and found with a white oil at 135°C that peroxides were the principal oxidation products. Carbonyl was next in order, with water and acids next. Only a trace of carbon dioxide was found. With lubricating oils Dornte used a temperature of 175°C and found that about 40 per cent of the oxygen was converted to water and 8 to 10 per cent to carbon dioxide.

Fenske *et al.*,[18, 19] who used a similar apparatus and technique, found that Pennsylvania lubricating oils are oxidized at 170°C to give the following distribution of oxygen in the oxidation products: water, 44 to 70 per cent; carbon dioxide, 3 to 9 per cent; carbon monoxide, 0.6 to 3.2 per cent; volatile acids, 1 to 7.5 per cent; fixed acids, 2 to 2 5 per cent; and 2 to 7 per cent isopentane insolubles, assuming that the latter contain 15 per cent oxygen. They found that the distribution of oxygen is influenced little by temperature over the range of 150 to 180°C, provided the amount of oxygen consumed is held constant, but that it varies as oxidation proceeds

Hicks-Bruun, Ritz, Ledley, and Bruun[23] made similar studies. They worked at a temperature of 175°C and found that 34.5 to 43.5 per cent of the oxygen could be accounted for as water, and 3 1 to 7.5 per cent as carbon dioxide. They compared an oil containing 19

per cent aromatic rings by Waterman analysis with one containin 3 per cent, and found that the former produced three to four time as much "soluble sludge" and "insoluble sludge" as the latter. Thi was of course to be expected, in view of the effect of aromatics a discussed earlier. They also found that the less aromatic oil formed more water and less carbon dioxide than the more aromatic sample. This again is consistent with the trend shown in Table 7.

Davis, Lincoln, Byrkit, and Jones[11] studied the oxidation of lubricating oils by measuring the pressure drop in a Sligh flask containing the sample of oil and oxygen, and fitted with a manometer.

TABLE 7 OXIDATION OF LUBRICATING OILS

Data from Larsen *et al*;[27] all values expressed as percentage of total oxygen consumed

	Temperature of Oxidation, °C	O_2 Absorbed, cc per 100 g	Free Acid	Combined Acid	Peroxide	Alcohol	Carbonyl	H_2O	CO_2	Volatile Acids	Asphaltene, mg per 10 g oil
40 VI* California	150	2826	5 0	11	0	2 9	1 5	36	21	2 4	135
50 VI California	150	3010	4.5	10	0	8.9	8 9	51	26	2 0	100
60 VI California	150	2853	4 7	12	0	2 5	1.4	56	12	1 7	65
70 VI California	150	2800	4 1	9 0	0	0 4	1 2	68	9 2	1 6	25
80 VI California	150	2803	3 8	10	0	.6	—	60	16	1 4	6
85 VI California	150	2800	4.1	12	—	1 3	2 5	65	16	1 2	2
Mid-Continent Neutral	150	3233	4.5	12·	< 1	0 7	5	49	—	1 1	—
Synthetic oil made from cracked wax olefins	150	2532	5 9	16	<1	9	9	34	7	2 4	0
	110	2980	6 6	15	0 4	8	19	26	4 9	3 8	0
White Oil	110	1571	13	19	5.0	13	44	11	—	1 3	0

* VI refers to Viscosity Index as defined by Dean and Davis

They showed that the oxidation products remaining in solution, after precipitation of the asphaltenes by the addition of naphtha, can be removed by adsorption, from naphtha solution, on a suitable clay. These oxidation products, which can be desorbed from the clay by means of a polar solvent such as acetone or alcohol, are termed resins. The de-resined oil, after removal of the naphtha, has virutally the physical properties of the original unoxidized oil This means of separation suggests the use of the resin content of a used oil as a good criterion of extent of oxidation, since it includes a large number of classes of oxidation products Such an application is, however, complicated by the fact that there is no sharp line of demarcation

between oil and resins or between resins and asphaltenes, but a more or less uniform series ranging from the least polar unoxidized hydrocarbon to the most insoluble asphaltene.

The oxidation of paraffin wax and of paraffinic oil fractions has received extensive study, largely by German and Russian investigators, for the purpose of producing fatty acids from petroleum.

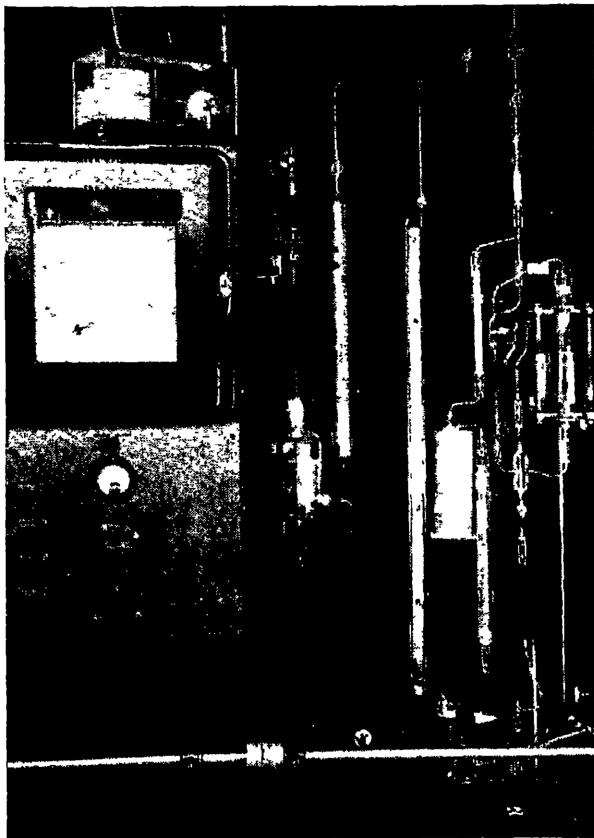


Figure 8. Oxygen Absorption Apparatus.

While the goal in such work is diametrically opposed to that of lubricating oil problems in that the purpose is to promote rather than stifle oxidation, the conditions used are comparable to those met by lubricating oils, and the products formed are of interest to those studying lubricating oils The German work has been reviewed by Gruse and Stevens.[20b] Yields of water-insoluble fatty acids up to

60 to 70 per cent are claimed. Oxidation, accomplished by blowing with air, may be done either in acid or alkaline medium, and various catalysts, including compounds of manganese, lead, mercury, chromium, vanadium, copper, and nickel, may be used. In addition to fatty acids of varying molecular weight, hydroxy acids, lactones, anhydrides, alcohols, aldehydes, ketones, and esters may be formed.

Similar conclusions were reached by the Russians. Likhushin, Masumyan, and Levkupulo[29] state that the oxidation of a wide fraction of fuel oil with air at 130°C will give yields as high as 41 per cent of acids. Higher yields are accompanied by excessive quantities of hydroxy acids. Sodium naphthenate was used as a catalyst. Danilovich and Dianina[10] prefer oxidation in four to five stages, with calcium naphthenate as catalyst, and report water-white fatty acids as products. Varlamov[39] studied the oxidation of Grozny paraffin at temperatures of 160 to 180°C with air at 15 to 30 atm pressure. From 20 to 74 per cent of the paraffin reacted, and 70 per cent or more of the oxidation products consisted of fatty acids of varying solubility. He found low molecular weight alcohols, aldehydes, and ketones in the volatile oxidation products. He also conducted some experiments in the absence of water, to determine whether this would influence the formation of hydroxy acids. He found, contrary to his expectations, that a high yield of acids could be obtained in the absence of moisture, and that a high percentage of the products consisted of hydroxy acids. He found manganese, copper, calcium, and nickel to be positive catalysts. Velikovskii and Lemer[40] oxidized paraffin and slack wax with air at a temperature of 160°C both in iron and in aluminum equipment. They found that the former metal favored the formation of insoluble hydroxy acids, particularly in the case of slack wax. With stepwise oxidation they were able to obtain maximum yields of acids, and a minimum of hydroxy acids Velikovskii and Vasil'eva[41] investigated the oxidation of various crude petroleum fractions, and found that in general reaction cannot be effected without a catalyst, but that oxidation could be accomplished with the aid of catalysts or by pretreatment of the oil with oleum. Calcium oleate was found to be an effective catalyst, and manganese oleate even more so. Petrov[31] describes a commercial process in which a petroleum distillate is sulfonated and the unsulfonated residue oxidized at 96 to 115°C in the presence of a calcium

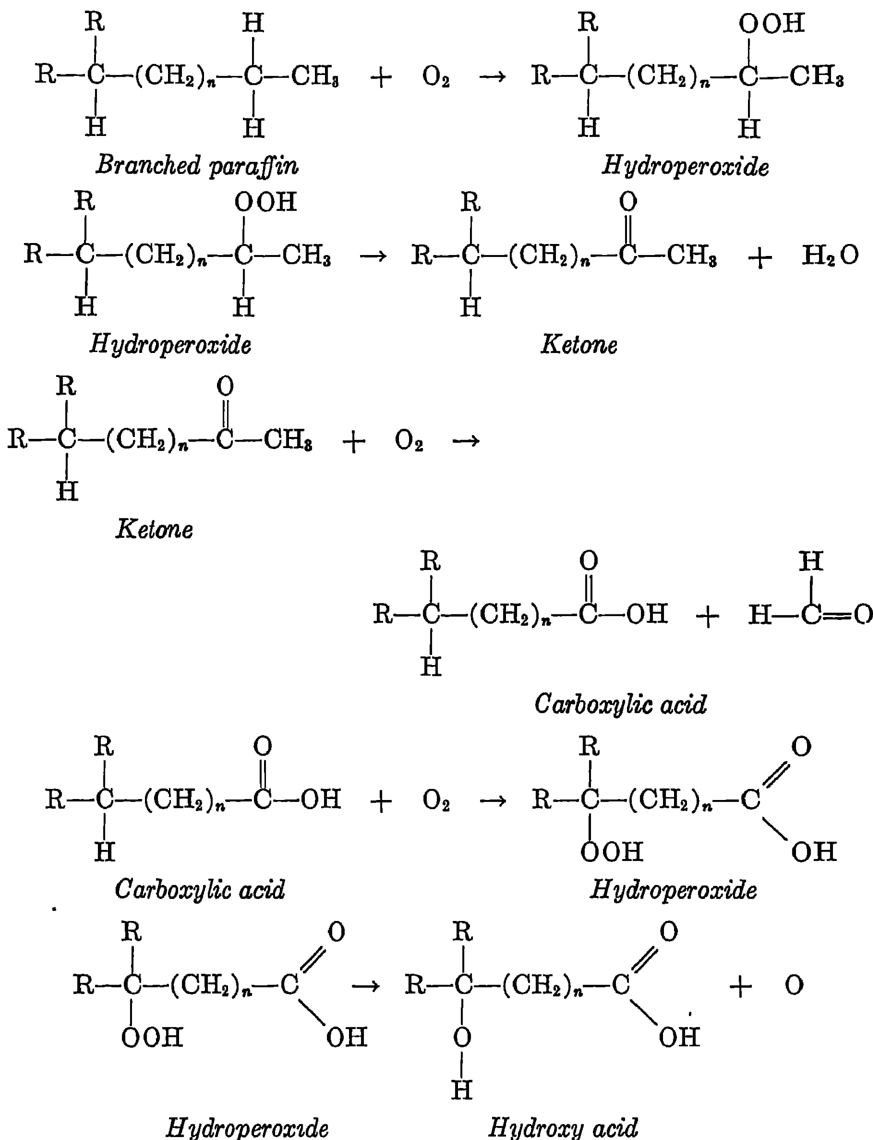
or manganese soap until a 20 per cent yield of fatty acid is reached.

Plisov, Golendeev, and Zel'tsburg[33] point out that the petroleum ether-insoluble hydroxy acids which are generally regarded as undesirable by-products in the manufacture of fatty acids, are valuable as film-forming substances in the lacquer and pigment industries, and as raw materials in the plastics industry. By oxidizing with air at 115 to 120°C they were able to obtain yields of 80 to 86 per cent of hydroxy acids, based upon total acids produced. They regard the product as a mixture of hydroxy acids, lactones, and lactides.

Shoruigin and Kreshkov[36] oxidized paraffin wax with air at 160°C and found the following products: water, hydroxy acids, lactides, and carboxylic acids and their anhydrides. The following straight- and branched-chain compounds, presumably hydroxy acids, were found: $C_{10}H_{20}O_3$, $C_{13}H_{26}O_3$, $C_{14}H_{28}O_3$, $C_{15}H_{30}O_3$, $C_{17}H_{34}O_3$ (two isomers), $C_{18}H_{36}O_3$, $C_{21}H_{42}O_3$ (two isomers), $C_{22}H_{44}O_3$, $C_{25}H_{50}O_3$, $C_{27}H_{54}O_3$, and $C_{32}H_{64}O_3$. The presence of beta-hydroxy acids was indicated.

Plisov[32] reports that Grozny paraffin, having a melting point of 52°C, is oxidized at 140 to 160°C to form peroxides which are capable of liberating iodine from potassium iodide and of oxidizing ferrous salts, and which are stable to heat. In addition, they report peroxides which are also stable, but which differ in that they do not respond to the usual test for peroxides Both types of peroxide are decomposed by acid or alkali, and they undergo hydrolysis by water. The last named reaction is catalyzed by calcium and sodium naphthenates.

The production of carboxylic acids from paraffin wax can be explained as outlined earlier. The paraffin is oxidized to the β-hydroperoxide, which decomposes to a methyl ketone, which in turn is oxidized further to formaldehyde plus a carboxylic acid containing one carbon less than the original paraffin. The formation of hydroxy acids may be associated with branched-chain paraffins Although Shoruigin and Kreshkov found both straight- and branched-chain compounds of the empirical formula $C_nH_{2n}O_3$, the majority of work reported indicates that paraffin wax shows less tendency to undergo oxidation to the hydroxy acid than do oil fractions or slack wax. The oxidation of a branched paraffin to an hydroxy acid could proceed according to the following mechanism:



Oxidation Rates

Pure Hydrocarbons. Larsen, Thorpe, and Armfield[28] have made an extensive study of the oxidation rates of a number of pure hydrocarbons. They measured oxygen absorption at 110°C, except in the case of the more stable compounds, which were oxidized at 150°C. Their results on thirty-nine hydrocarbons, representing paraffins,

TABLE 8. OXIDATION RATES OF PURE HYDROCARBONS
Data from Larsen, Thorpe, and Armfield[28]

Hydrocarbon	Oxid Temp., °C	Time to Absorb 2000 cc of O_2 per Gram-Mole, hr	Type of Curve (See Fig 6)
1. Tetralin	110	1.5	2
2 Tetraisobutylene	110	2	3
3 Octahydroanthracene	110	2	4
4 9,10-Dihydro-9,10-diisobutyl-anthracene	110	2 5	2
5. *n*-Octadecylbenzene	110	2.5	3
6. *β*-*n*-Octadecyltetralin	110	3 5	4
7 Polyisobutylene, $(C_4H_8)_{13}$	110	4	3
8. *α*-Phenyl-Δ^2-tetralylbutane	110	7	4
9 9,10-Diisobutylperhydroanthracene	110	7	1
10. 5-Isobutylacenaphthene	110	8	2
11 *n*-Hexadecylbenzene	110	12	4
12 Perhydroanthracene	110	12	1
13. Hydropolyisobutylene, $(C_4H_8)_{13}H_2$	110	17	4
14 Hexaethylbenzene	110	23	1
15. *β*-*n*-Octadecyldecalin	110	24	1
16. Fluorene	110	26	2
17 Decalin	110	27	1
18 Dicyclohexyl	110	28	1
19. *n*-Amylcyclopentane	110	28	1
20. *n*-Amylbenzene	110	28	3
21. 1-*α*-Naphthyl-1-*n*-butylhexadecene	150	2	3
22 *n*-Octadecylcyclohexane	110	37	1
23. *n*-Hexadecylcyclohexane	110	45	1
24. Cetane	110	45	1
25. *n*-Decane	110	47	1
26. *sec*-Amylbenzene	110	68	1
27. *tert*-Amylbenzene	110	85	1
28. Benzylnaphthalene	110	120	3
29. Diphenylmethane	110	>70	2
30. Di-*α*-naphthylmethane	150	12	1
31. *α*-*n*-Octadecylnaphthalene	150	33	1
32 Poly-*sec*-amylnaphthalene	150	42	1
33 *α*-Isoamylnaphthalene	150	55	2
34. *α*-Methylnaphthalene	150	62	2
35. Di-*sec*-amylnaphthalene	150	72	3
36 *β*-*sec*-Amylnaphthalene	150	140	1
37. *β*-Methylnaphthalene	150	>150	3
38. *tert*-Butylnaphthalene	150	>150	3
39 Naphthalene	150	>150	3

olefins, naphthenes, benzene and naphthalene aromatics, and combinations of these types in the same molecule, are summarized in Table 8 For the sake of brevity the compounds are classified in this tabulation only according to the time required to absorb 2000

cc of oxygen per gram-mole and according to the type of curve obtained, as defined in Figure 9. (It should be understood that the "type of curve" applies only under the given set of conditions. von Fuchs and Diamond[42] have shown that a given oil may exhibit autocatalysis or autoretardation, depending upon the temperature

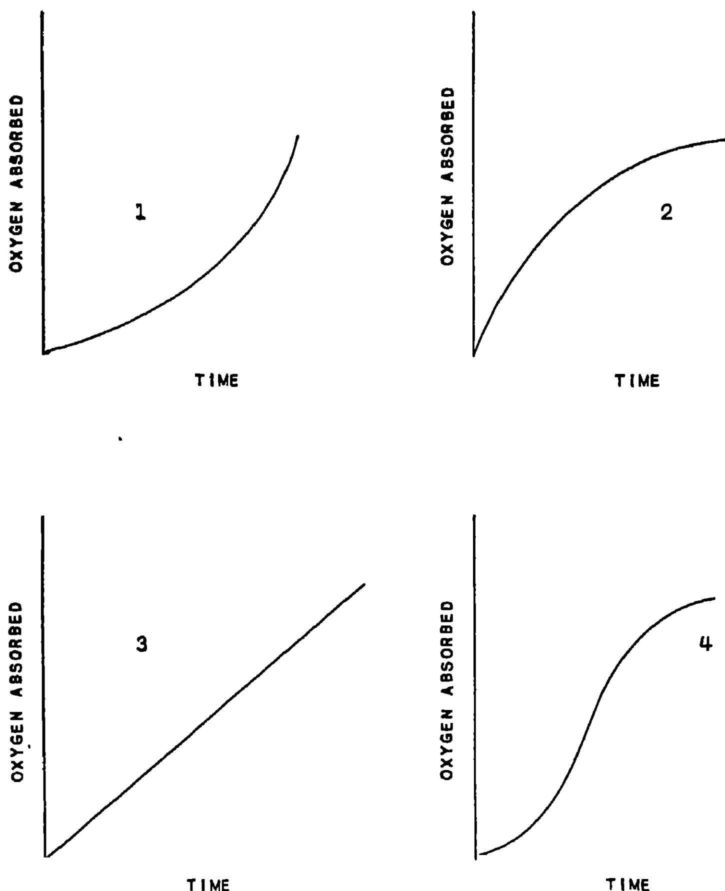


Figure 9. Types of Curves Referred to in Table 8

of oxidation.) Two thousand cc of oxygen per gram-mole corresponds to the oxidation of approximately 9 per cent of the molecules with one molecule of oxygen per molecule of hydrocarbon, or 4.5 per cent with two molecules of oxygen. It will be recalled that one molecule is required to convert a paraffin to a peroxide or ketone, and an additional molecule to convert the ketone to a carboxylic acid plus a low molecular weight aldehyde For a lubricating oil with

a molecular weight of 400, the figure of 2000 cc per gram-mole corresponds to 500 cc per 100 g. The four types of curve are the autocatalytic, the autoretardant, the linear, and the combination type in which autocatalysis prevails first, then autoretardation. Table 8 lists the hydrocarbons in order of increasing stability. In comparing two compounds oxidized at different temperatures, a factor of 16 was used to convert the rate of oxidation at 110°C to that at 150°C This factor is based upon a doubling of reaction rate per 10°C and is not strictly correct, but sufficiently close for the purpose of comparison.

It will be observed that the ten paraffins, naphthenes, and alkylnaphthenes all had "2000 cc times" between 12 and 47 hours at 110°C, and all showed the autocatalytic type of curve, at least in the early stages (type 1 or 4) The most rapid oxidation was shown by hydrocarbons containing either a double bond, a partially hydrogenated condensed ring, or a benzene ring with a long paraffinic side chain. Surprisingly, these compounds, eleven in number, which had "2000 cc times" ranging from 1.5 to 12 hours at 110°C do not in general give an autocatalytic type of oxidation curve. Only one gave a type 1 curve, and four a type 4 The other six were equally divided between types 2 and 3. Thus autocatalysis is not a requisite for rapid oxidation. The naphthalene derivatives were as a class the most stable, and most of their oxidation curves were of either the autoretardant or the linear type.

The effect of olefinic unsaturation is brought out by a comparison of items 7 and 13. The latter, hydropolyisobutylene, was obtained by hydrogenation of the former, polyisobutylene, which contained one C=C bond per C_{52} molecule. The paraffin had a "2000 cc time" of 17 hours, which is more than four times that of the olefin.

Hydrogenation of an alkylbenzene to the corresponding cyclohexane derivative resulted in an increase in stability, as shown by comparing item 5 with 22, and 11 with 23. The effect was to increase the "2000 cc time" by factors of 15 and 4, respectively, which are of the same order as that found in the case of the olefin. Both of these alkylbenzenes had long side chains (C_{16} and C_{18}), and the effect of hydrogenating benzene itself or a low molecular weight homolog would probably be quite different.

Hydrogenation of a naphthalene ring, on the other hand, results in a marked loss of stability, particularly if the naphthalene ring is

only partially hydrogenated. The most stable hydrocarbon listed in Table 8 is naphthalene, with a "2000 cc time" of >150 hours at 150°C or >2400 hours at 110°C, assuming the above-mentioned factor of 16 for the difference in temperature of 40°C. Tetrahydronaphthalene, or tetralin, is on the other hand the least stable compound shown in Table 8 It has a "2000 cc time" at 110°C of only 1.5 hours. Thus the partial hydrogenation of naphthalene reduced its stability by a factor of more than 1600. Complete hydrogenation to decahydronaphthalene, or decalin, brings the "2000 cc time" back to 27 hours, which is 18 times that of tetralin, but still short of that of naphthalene by a factor of >89. That chain length does affect the influence of hydrogenation of the naphthalene ring is shown by comparing the above results with a comparison of items 31, 15, and 6, which represent the octadecyl derivatives of naphthalene, decalin, and tetralin, respectively, although unfortunately, for purposes of the present comparison, the first is the alpha derivative, and the other two the beta. Octadecylnaphthalene had a "2000 cc time" at 150°C of 33 hours, which would correspond to 530 hours at 110°C, and the tetralin and decalin derivatives 2.5 and 24 hours, respectively, at 110°C. Thus the factors relating the "2000 cc time" of the naphthalene to that of the tetralin and decalin derivatives are 530/2.5 and 530/24, or 210 and 22, respectively. The differences between these values and the corresponding ones of >1600 and >89 for the unsubstituted homologs are probably due primarily to the effect of the alkyl group rather than the difference in position.

Item 21, 1-α-naphthyl-1-n-butylhexadecene, is interesting in that it contains both a naphthalene group, which would classify it with the stable hydrocarbons, and olefinic unsaturation, which would classify it with the unstable compounds. The two effects seem to balance each other, with the result that this compound has an intermediate stability comparable to that of the paraffins and naphthenes.

Comparison of items 20, 26, and 27 is of interest in that these three compounds are primary, secondary, and tertiary amyl derivatives of benzene, respectively, and hence show the influence of the structure of the side chain. According to the mechanism proposed earlier for the oxidation of an alkylbenzene, the first of these three bydrocarbons would form the hydroperoxide at the alkyl carbon attached to the ring. The peroxide would then dehydrate to phenyl autyl ketone. The second would likewise form the peroxide, but,

since there was only one hydrogen atom on the carbon in question initially, propyl alcohol, rather than water, would split off, and acetophenone would be the other product. Since this process involves the breaking of a C—C bond, whereas the first does not, it is not surprising that the "2000 cc time" for the primary compound is less than half that for the secondary (28 hours compared to 68). Furthermore, since the tertiary compound cannot form a hydroperoxide at the carbon attached to the ring, but must oxidize at other positions, it would be expected to be the most stable of the three, and this was again the case, for the "2000 cc time" for *tert*-amylbenzene was 85 hours. A similar trend was noted by Stevens and Roduta,[38] who found *tert*-butylbenzene much more resistant to oxidation than any of the other alkylbenzenes which were examined (see Table 5). The extreme stability of *tert*-butylnaphthalene as compared to the other naphthalenes (see item 38, Table 8) is also in line with this trend.

Larsen, Thorpe, and Armfield[28] attribute the extreme stability of naphthalene aromatics in comparison with benzene homologs to the difference in the effectiveness of their oxidation products as inhibitors (naphthols in the one case versus phenols in the other. To support this theory, they oxidized *n*-amylbenzene (item 20, Table 8) to which had been added 9.8 per cent of preoxidized α-methylnaphthalene. The curve of the mixture was practically coincident with that for α-methylnaphthalene itself (item 34). This represents a 35-fold increase in "2000 cc time," assuming again a factor of 2 per 10°C in change in temperature.

Chernozhukov and Krein[7] did not determine rates of oxidation, since most of the compounds they studied were oxidized in a bomb for a fixed time. It is possible, however, to compare the behavior of various compounds under identical conditions and thus determine relative stability. They found that naphthalene, anthracene, and biphenyl, after 3 hours at 150°C and 15 atm of oxygen, had zero saponification values, whereas α-methylnaphthalene, β-methylnaphthalene, and propylnaphthalene produced, under these same conditions, saponification values of 12, 16, and 49, respectively. From this the authors conclude that chainless polynuclear aromatics are very stable, that the introduction of side chains, particularly long side chains, decreases stability, and that the beta derivatives of naphthalene are more reactive than the alpha. They also found that

the presence of an intermediate link of carbon atoms between two aromatic rings, as in diphenylmethane, lowers stability. All these conclusions are in agreement with those of Larsen, Thorpe, and Armfield, except that regarding the relative stability of α- and β-methylnapththalenes Chernozhukov and Krein found, as did Larsen *et al.*,[27] that benzene derivatives are less stable than naphthalene homologs, and that the higher alkyl compounds are less stable than those of lower molecular weight. For example, after oxidation at 110°C and 15 atm of oxygen for 3 hours, 1,3,5-trimethylbenzene had a saponification number of 11, whereas propyl-, nonyl-, decyl-, *p*-methyl-, isopropyl-, and *o*-methylisopropylbenzenes had saponification numbers ranging from 31 to 48 after oxidation under the same conditions.

Balsbaugh and Oncley[2] studied the oxygen absorption of tetralin, decalin, and cetane at 30, 75 and 100°C, respectively, and found these three hydrocarbons to rate in the order of increasing stability in which they are mentioned. This is the same order shown for these compounds in Table 8.

Hock and Lang[24] found that cyclopentene is oxidized at a slower rate than cyclohexene, and hydrindene, which can be regarded as tetralin minus one CH_2 group, at a slower rate than tetralin; from these results they conclude that a five-membered ring is less readily oxidized than a six-membered ring. However, their conditions differed from those used by others quoted above in that they used oxygen plus ultraviolet light. Their results cannot, therefore, be compared with the others without reservation.

Mixtures and Petroleum Fractions. When two hydrocarbons of unequal stability are blended, an intermediate stability might be expected, with the component of lower stability being oxidized preferentially. Actually a blend may possess a stability considerably greater than that of either component, and the least stable component is not necessarily oxidized in preference to the more stable one. Thus the stability of a blend of a few hydrocarbons or a mixture of several is probably determined to a large extent by interaction phenomena among various molecules or radicals This, of course, greatly complicates the problem.

It was pointed out earlier in the chapter that the oxidation products of a lubricating oil resemble those of substituted naphthalenes, and that this class of hydrocarbons may, therefore, be oxidized pref-

erentially in a blend, even though by themselves such compounds are exceedingly stable. This point is brought out in greater detail in Table 9, which shows the effect of the addition of diamylnaphthalene to a white oil upon the distribution of oxidation products. The average data for naphthenes and alkylnaphthenes, to which class a white oil would belong, and for naphthalene derivatives, including diamylnaphthalene, are repeated from Table 6 for comparison.

Of the six oxidation products listed, three—namely, free acid, peroxide, and carbonyl—show appreciably lower values for the naphthalene than for the naphthene, and one, water, behaves in the opposite manner. Alcohols and combined acids or esters are produced

TABLE 9. EFFECT OF THE ADDITION OF DIAMYLNAPHTHALENE TO A WHITE OIL UPON THE DISTRIBUTION OF OXIDATION PRODUCTS

Data from Larsen *et al*,[27] all figures expressed as percentage of total oxygen consumed

	Free Acid	Combined Acid (Ester)	Peroxide	Alcohol	Carbonyl	H_2O
Average naphthene or alkylnaphthene	11	17	14	8.9	51	22
White Oil (mol. wt. = 387)	13	20	5	13	44	17
White Oil + 12.5% diamylnaphthalene	16	22	2.6	5.1	33	21
White Oil + 25% diamylnaphthalene	9	23	0.2	6.4	14	24
White Oil + 50% diamylnaphthalene	5.7	28	0.3	8.0	—	57
Average naphthalene derivative.	7	16	1.4	9.0	10	51

to about the same extent in both classes of compounds. It is significant that as the percentage of diamylnaphthalene in white oil is increased from 0 to 50 per cent the percentage of oxygen appearing as free acid, peroxide, and carbonyl decreases progressively, and the percentage appearing as water increases accordingly. It would appear that in blends of 25 to 50 per cent of diamylnaphthalene in white oil, the former is oxidized preferentially, even though white oil has a "2000 cc time" at 130°C of about 5 hours, compared with 72 hours at 150°C for diamylnaphthalene, or 288 hours at 130°C, which means that by itself, the white oil is fifty-eight times as reactive as diamylnaphthalene.

That a blend of two components may be more stable than either

by itself is brought out clearly in an example cited by von Fuchs and Diamond,[42] who measured the time required for the absorption of 1800 cc of oxygen per 100 g of oil for a motor oil containing varying quantities of bright stock aromatics. Oxidation was effected in the presence of iron as a catalyst. They found that the curve relating absorption time to concentration of added aromatics passed through a distinct maximum in the vicinity of 5 per cent, dropping off to absorption times less than half of the maximum at 0 and 10 per cent. Thus this blend has a definite "optimum aromaticity." The concept of optimum aromaticity is of great practical importance; it, along with the more conventional criteria of Viscosity Index and yield, determines the proper degree of solvent extraction to which a given stock should be subjected.

That lubricating oils possess an optimum aromaticity with respect to stability was also found by Fenske *et al.*,[18] who separated a Pennsylvania oil, containing 9 per cent of aromatic rings, into 124 fractions by a combination of vacuum distillation and solvent extraction. They studied the rate of oxidation of seven of the fractions, ranging in aromaticity from 0 to 40 per cent aromatic rings, along with the original material. They used a temperature of 140°C in a conventional oxygen-absorption apparatus, and found that none of the fractions examined was as stable as the original oil. Two fractions of zero aromaticity were the least stable, with one containing 2 per cent aromatic rings next, two of 37 and 40 per cent next, and two of 15 and 25 per cent the most stable, except for the original oil. That this was not caused by damage inflicted in the processing was proved by an oxidation test on a blend of all 124 fractions in the original proportions, which checked the run on the original sample.

An optimum aromaticity for insulating oils is indicated in the work of Clark,[9] who studied the dielectric stability (which is known to be closely related to oxidation stability) of a series of oils with varying olefinic and aromatic unsaturation. Olefinic unsaturation was determined by absorption in sulfuric and boric acids, and aromatic plus olefinic unsaturation in sulfuric acid and phosphorus pentoxide, both according to Kattwinkel. Clark found a sharp and progressive decrease in dielectric stability with increasing olefinic unsaturation over the range of 0 to 6 per cent; however, variation in aromatic unsaturation from 0 to 12 per cent showed a maximum stability in the vicinity of 6 per cent.

von Fuchs and Diamond[42] found that the shape of the rate curve can be drastically altered by the concentration of added aromatics and by temperature. This necessitated a revision of the theory proposed by Dornte *et al.*[13, 14, 15] who classified oils into three groups: those whose oxidation products were (1) positive catalysts, (2) negative catalysts, or (3) without any catalytic effect. von Fuchs and Diamond concluded that aromatics can possibly "act in a twofold capacity—i.e., both as inhibitors and retardants; either several compounds present may be acting differently or the same compound may be playing a dual role. At low concentrations conventional inhibitor action outweighs the other and an induction period is observed; at higher concentrations this effect is obscured by the additional quantity of aromatics, and autoretardation predominates. At intermediate concentrations the opposing tendencies of autocatalysis and autoretardation are balanced against each other more evenly so that the rate curve may possess an intermediate curvature or even be linear."

Larsen, Thorpe, and Armfield[28] studied the effect of adding naphthalene derivatives to other substances, and found a stabilizing effect. A much greater effect was, however, obtained when the naphthalene compound was preoxidized in the absence of the other component. They attribute these results to the fact that in the former case oxidation of the naphthalene compound and oxidation of the second component are competitive, whereas in the latter the oxidation products of the alkylnaphthalene, probably naphthols, are present as antioxidants throughout the oxidation of the blend.

The effect of added aromatics upon the oxidation of paraffins and naphthenes has also been investigated by Chernozhukov[6] and by Chernozhukov and Krein,[7,8] who regard the stability of mineral oils to be determined essentially by the character and quantity of the aromatics present. They found, for example, that the addition of 1 to 10 per cent of naphthalene, phenanthrene, or anthracene to a vaseline oil resulted in a marked improvement in stability, according to their oxygen bomb test They show this to be due to a preferential oxidation of the aromatics, with the oxidation products acting as antioxidants They obtained similar results, though to a lesser degree, with substituted aromatics. This order of effectiveness of the substituted and unsubstituted aromatics in increasing the stability of a blend is the opposite of that found by Larsen, Thorpe, and

Armfield,[28] who found naphthalene ineffective in altering the oxidation curve of decalin, whereas substituted naphthalenes are effective. It must be remembered, however, that the conditions used in the two laboratories were different.

Denison[12] does not concur with Chernozhukov and others in their views on the importance of aromatics in determining the stability of a mineral oil. He considers natural sulfur compounds, rather than the hydrocarbon composition, to be the important factor. His conclusions are based on oxygen-absorption measurements on three oils before and after desulfurization, which was effected by treatment with metallic sodium in the presence of hydrogen at a pressure of 200 psi and at a temperature of 500°F. His results are summarized in Table 10.

TABLE 10 EFFECT OF DESULFURIZATION UPON STABILITY AND PROPERTIES
Data from Denison[12]

Oil	Time To Absorb 100 cc O_2 per 100 g, hr	Sulfur, %	Specific Dispersion	Per Cent Aromatic Rings (Waterman)
California naphthenic SAE-30	0 7	0 53	120	15
California naphthenic SAE-30, desulfurized	2	07	121	14
California paraffinic 400 neutral	5.0	22	106	1
California paraffinic 400 neutral, desulfurized	>0.1	06	—	1
Pennsylvania SAE-30	2 5	.10	111	7
Pennsylvania SAE-30, desulfurized	0 1	01	110	4

Denison reasons that since desulfurization resulted in little change in the hydrocarbon content of the oil, as shown by specific dispersion and Waterman analyses, and by the fact that no olefinic unsaturation was indicated by bromine number determinations, the decrease in stability was due solely to the removal of sulfur, and that "natural sulfur compounds seem to be the agents responsible for the stability of straight mineral oils." However, a glance at Table 10 shows that, if this is the case, the relationship between stability and sulfur content is not a simple function, for the Pennsylvania oil, which was lowest of the three in sulfur both before and after treatment, was in both cases intermediate in stability, while the California naphthenic, which was highest in sulfur, was the least stable of the three before treatment, and the most stable after. Furthermore, the process of desulfurization necessarily alters the hydrocarbon structure. The

sulfur was presumably removed by decomposition, with the rest of the molecule remaining in the oil. Since 2 to 20 per cent of the original oil consisted of sulfur compounds, it is scarcely conceivable that the changes in hydrocarbon structure do not affect stability. It is possible that a small amount of olefinic unsaturation escaped detection in the bromine number determination, since this analytical method is known to be less reliable for complex molecules as found in a lubricating oil than for the simpler olefins for which the method was devised. There is, moreover, a possibility that some reaction between sodium and aromatic rings took place, with the subsequent formation of tetralin-type compounds. Gilman, in his "Organic Chemistry," reports that naphthalene can be reduced to tetralin by the action of sodium in liquid ammonia solution. It is conceivable that a similar reaction occurred under the conditions used by Denison. While the extent of such reactions could not have been great, since specific dispersion was not affected appreciably, the presence of a small amount of tetralin or related compound would be expected to have a profound influence on stability. It will be recalled from the discussion of Table 9 that tetralin is more than 1600 times as reactive as naphthalene. Furthermore, tetralin forms copious quantities of peroxides[2] which probably act as prooxidants, whereas naphthalene forms naphthols which act as antioxidants.[42]

In view of this analysis of the problem, it would appear that the relative importance of aromatics and sulfur compounds in determining the rate of oxidation of straight mineral oils cannot be stated definitely without further experimentation. Both are probably involved, rather than either one alone. In addition, compounds containing other elements, notably oxygen and nitrogen, and which occur naturally in the lubricating oil fraction of petroleum, undoubtedly play a role in determining the stability of an oil.

Effect of Catalysts and Inhibitors. All the oxidation studies discussed thus far, with the exception of a few cases where catalysts were specifically mentioned, have been in the absence of added catalyst or antioxidant. In actual practice either of these classes of material can, and usually does, have a profound effect upon the rate of oxidation of a lubricating oil.

Catalysts for the oxidation of lubricating oil include a wide variety of compounds. Hanson and Egerton[21] report that nitrogen dioxide, in concentrations comparable to that present in engine cylinders,

greatly influences the rate of oxygen absorption of an oil at 220°C, the effect being that of shortening the induction period. Oxidation products, notably peroxides, may themselves be catalysts, as evidenced by the concave-upward, or autocatalytic, type of oxygen-absorption curve exhibited by certain oils under certain conditions. However, these do not constitute the most serious source of catalysis of deterioration encountered by lubricating oils Metal catalysis, principally by compounds of metals which can readily change valence and specifically by compounds of copper, lead, and iron, is always to be reckoned with. These three metals are probably no worse in their effect than several others which could act as catalysts, such as manganese, chromium, or vanadium, but they play a more important role because of their much greater prevalence: copper in the form of oil lines, brass fittings, and bearing metal; lead as bearing metal and as a constituent of the decomposition products of tetraethyllead; and iron as the major constituent of the engine itself.

Davis, Lincoln, Byrkit, and Jones[11] showed that the naphthenates of iron, lead, copper, cadmium, and silver all act as catalysts for the oxidation of lubricating oil, the effect varying with concentration. They found that in general an oil can "tolerate" a certain amount of catalyst without any appreciable effect upon rate of oxidation, but that an increase in concentration beyond this threshold value results in a marked decrease in induction period. As the concentration is increased further, a point is eventually reached where the system is again insensitive to further change in concentration. For example, a Mid-Continent, vacuum-distilled, solvent-refined oil had an induction period of 80 min at 175°C. The addition of iron naphthenate up to 0.006 per cent as Fe_2O_3 had no effect, but further addition to 0.1 per cent resulted in a linear decrease in induction period. on a log-log plot, to less than 20 min. Further addition of iron naphthenate was without noticeable effect. All this work was done in a static system, and measurements were limited to the initial phases of oxidation, so that the conclusions reached need not necessarily apply under conditions of agitation of the oil and oxidation to a greater extent. It would appear, however, that oils contain natural "anticatalysts" which are capable of nullifying the effect of a certain amount of added catalyst, and that at high concentrations of metal soap the system reaches a state of catalytic saturation.

Fenske *et al.*,[18] who used a conventional circulatory oxygen-ab-

sorption apparatus, studied the effect of copper, iron, and lead, both in metallic and in soluble naphthenate form. They found copper naphthenate to be the most potent of the three soaps, and lead the least. This same order prevailed for the bulk metals in the early stages of oxidation, but in the later stages, lead became the most potent of the three. This was attributed to the greater solubility of lead compounds in the oil, as compared with those of iron and copper. Fenske also found that catalysis by these metals has little effect in altering the distribution of oxidation products, the main effect being that of increasing the over all rate of oxidation rather than that of any one specific reaction.

Larsen and Armfield[26] studied these same three catalysts, both in soluble and in bulk metal form, in three different oils, and at varying concentrations of soluble naphthenate and ratios of surface of metal to volume of oil. Their results with an extracted Mid-Continent oil were essentially in agreement with those reported by Fenske. Five and one-tenth sq cm of copper per gram had approximately the same catalytic effect as 14.1 sq cm of iron per gram, indicating the former metal to be the more active of the two on a basis of equal areas per gram of oil. Three sq cm per gram of lead was much less active than either copper or iron in the early stages, but became equal to them when 800 cc of oxygen per 100 g of oil had been absorbed. From there on it was the most active of the three metals. They found 100 ppm of copper, 500 ppm of lead, and 1000 ppm of iron, all in the form of naphthenate, to have about the same catalytic effect. This order differs from that reported by Fenske in that the positions of lead and iron naphthenates are reversed.

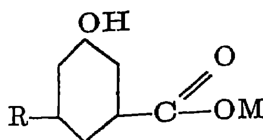
In their study of the effect of surface area of metal and concentration of soluble metal, Larsen and Armfield found that curves of varying forms were obtained, depending upon the catalyst and upon the oil. They showed, for example, that three oils, a California extracted, a Mid-Continent extracted, and a Pennsylvania, could be rated in all six of the possible orders of stability at a given temperature (150°C) and with a given catalyst (copper naphthenate), merely by altering the concentration of dissolved copper. Thus, if an oxidation test is to have significance in terms of correlation with engine behavior, the choice of catalyst, with respect to both kind and amount, must be judicious.

Larsen and Armfield[26] studied catalysis in engines by withdrawing

oil samples and determining their rate of oxidation in glass without any other added catalyst. They found that an oil loses stability very rapidly, particularly if the engine is operating without a filter. They found that a used oil could be considerably improved with respect to stability simply by filtration. Removal of fuel dilution by steam distillation had little further effect, but removal of soluble metals by washing with dilute hydrochloric acid and percolation through clay restored the oil practically to its original stability. They showed that the oil insolubles, or "crankcase catalyst", constitute a potent catalyst, particularly when obtained from an engine which operated on a leaded gasoline. The copper and lead contents of crankcase catalyst are too low to account for its activity, which the authors believe is due to the presence of iron halides, derived from engine metals and the halogen compounds present in tetraethyllead fluid.

While heavy petroleum fractions have been in the past, and still are to a certain extent, used as such, the trend is toward the incorporation of additives for various specific purposes. These include, among others, dispersants, metal passivators and deactivators, and conventional antioxidants. The last-named class is, of course, of the greatest concern here, but the others cannot be ignored in oxidation studies, for they may have a profound, though indirect, effect upon rate of oxidation. Dispersants, for example, peptize certain oxidation products and keep them colloidally dispersed, thus preventing their deposition as lacquer. In this manner they keep the metal surfaces of an engine clean, but vulnerable to attack by acidic oxidation products of the oil or fuel The dissolved metals then act as catalysts for further oxidation. Passivators, on the other hand, protect metal surfaces from attack by forming a protective film on their surface, and thus prevent metal catalysis as well. Deactivators nullify the catalytic effect of dissolved metals by reacting with them and forming a nonactive, or sometimes an insoluble, combination. Thus, dispersants, passivators, and deactivators, none of which need have any effect upon oxidation rate in glass and in the absence of catalysts, may have a large effect in engines.

A single compound may serve in more than one capacity. Reiff[35] has shown that metal salts of phenolic acids of the following general structure have multi-functional properties. M is a metal and R an alkyl group. Compounds of this class act as pour-point depressors



and Viscosity-Index improvers. They are also inhibitors, as shown by the fact that viscosity increase, naphtha insolubles, and neutralization number are maintained at a low value in engine tests as compared to a blank run on the oil without additive.

Since the pioneer work of Moureu and Dufraisse,[30] antioxidants have been investigated for stabilizing a number of products, including rubber, fats, chemicals, and gasoline, as well as lubricating oil. A complete review of this field is beyond the scope of this chapter and only a few references will be cited.

The mechanism of the action of antioxidants is generally considered to be that of chain breaking, the antioxidant reacting with a "hot" molecule and thus being itself oxidized. In this process the antioxidant molecule is destroyed, but with a dissipation of the energy possessed by the "hot" molecule, so that the chain is broken. Thus the oxidation of hundreds or thousands of molecules of hydrocarbon has been prevented, since this energy is passed on from one molecule to the next in the normal chain reaction.

One of the earliest studies of antioxidants in mineral oil was reported by Haslam and Frolich[22] in 1927. They tested a number of compounds, most of which contained nitrogen, in 0.01 per cent concentration in a medicinal oil by bubbling dry oxygen through the oil at a temperature of 130°C, and followed the course of oxidation by measurements of neutralization number. The following compounds, listed in order of increasing potency, were found to be effective. diphenylguanidine, β-naphthylamine, ethyl-α-naphthylamine, *p*-aminophenol, diphenylamine, phenyl-α-naphthylamine, and unsymmetrical diphenylhydrazine.

Fenske *et al.*[18] classify antioxidants as: (a) hydroxy compounds (phenols, naphthols); (b) nitrogen compounds (amines, etc.); (c) sulfur compounds (disulfides, thioethers, etc.); (d) organometallic compounds; (e) halogen compounds; (f) compounds containing higher members of the nitrogen and oxygen groups in the Periodic Chart, such as phosphorus, arsenic, antimony, selenium, and tellurium.

Dornte[13] showed that the addition of 0 01 per cent of phenyl-α-

naphthylamine to a white oil increased its induction period from practically zero to about 20 hours, after which the oxidation curve was practically parallel to the curve for the original oil. von Fuchs and Diamond[42] found that a turbine oil base stock, which approached white oils in degree of refining, responded to the addition of phenyl-α-naphthylamine in a similar fashion. On the other hand, less severely treated oil, e.g., solvent-extracted neutrals, displays a far inferior susceptibility to this inhibitor. Thus the addition of antioxidant, at least of the phenyl-α-naphthylamine type, to an oil is by no means a universal "cure-all." The base stock to which it is added must be carefully refined, not for maximum stability, but for maximum inhibitor susceptibility.

Chernozhukov and Krein[7] investigated several compounds as antioxidants in their bomb test, and found catechol, hydroquinone, resorcinol, pyrogallol, quinone, aniline, and β-naphthylamine to be effective. Resins obtained from petroleum fractions by extraction with acetone were also effective. These were probably similar in character to the bright stock aromatics previously mentioned which were reported by von Fuchs and Diamond[42] as increasing the stability of a motor oil when added in low concentration. Chernozhukov and Krein also report favorable preliminary results on several organic sulfur compounds, but do not list the compounds tested.

Denison and Condit[12a] studied a series of organic selenium compounds as antioxidants and found many of them, e.g., dicetyl selenide, to be much more effective than the corresponding sulfur compounds. They proposed a mechanism in which the selenide, R-Se-R, reacts with organic peroxides to form a selenone, $R\text{-}\overset{\overset{O}{\|}}{Se}\text{-}R$, and in which the latter subsequently breaks down to form, along with other products, half of the original dialkyl selenide.

Commercial practice in the use of antioxidants depends to a considerable degree upon the manufacturer and upon the application intended for the lubricant. Since oils differ widely in their susceptibility to antioxidants, it is necessary to select a combination of base stock and additive which will result in a stable product.

Turbine oils are commonly stabilized by the addition of β-naphthol, phenyl naphthylamine, or phenol derivatives, e.g., 2,6-ditertiary-butyl-4-methyl phenol.[24a] Antioxidants used in motor oils included the following compounds and types:[20a, 24a] tributyl phos-

phite, triphenyl phosphite, tri-p-tertiary-amylphenyl phosphite, alkyl phenol sulfides and their calcium derivatives, sulfurized fatty oils, zinc methylcyclohexyldithiophosphate, reaction product of phosphorus pentasulfide and pinene, tetramethyldiaminodiphenylmethane, calcium cetyl phenate, and alizarin. Many of these additives act as corrosion inhibitors as well as reducing the rate of oxidation. Furthermore, antioxidants are frequently used in conjunction with other additives. Turbine oils, for example, usually contain rust inhibitors, and motor oils, particularly "heavy duty" oils often contain dispersants.

Bibliography

1. Baker, M. D., *Power*, **85**, 314–7 (1941).
2. Balsbaugh, J. C , and Oncley, J. C., *Ind. Eng. Chem.*, **31**, 318–26 (1939).
3. Burwell, A. W , "Science of Petroleum" Vol **II**, pp. 1028–32, London, Oxford University Press, 1938
4. Chavanne, G , and Bode, E , *J. Am Chem. Soc* , **52**, 1609–22 (1930).
5. Chavanne, G , and Tock, G., *Bull. soc chim Belg* , **41**, 630–47 (1932)
6. Chernozhukov, N. I., *2me Congr. mondial pétrole*, **2**, Sect. 2, 797–802 (1937).
7. Chernozhukov, N. I , and Krein, S. E , *J Applied Chem* (*U.S S R*), **10**, 1435–8 (1937); *Chem Abstracts*, **32**, 1664 (1938).
8. Chernozhukov, N I , and Krein, S E , *Neftyanoe Khoz*, **23**, 242–50, 285–90 (1932); **25**, 35–8, 102–5 (1933); **28**, 59–66 (1935), *Foreign Petroleum Technol.*, **1**, 121–34 (1933); **2**, 21–80 (1934), **3**, 577–94 (1935), **4**, 13–32 (1936).
9. Clark, F M., *Ind. Eng. Chem* , **31**, 327–33 (1939).
10. Danilovich, A , and Dianina, T., *Masloboĭno Zhirovoe Delo*, **1935**, 15–18, *Chem Abstracts*, **29**, 5255 (1935)
11. Davis, L L., Lincoln, B. H , Byrkit, G D , and Jones, W A , *Ind. Eng Chem* , **33**, 339–50 (1941).
12. Denison, G. H., *Ind. Eng. Chem.*, **36**, 477–82 (1944).
12a. Denison, G H., and Condit, P C., *Ind Eng Chem.*, **41**, 944–8 (1949).
13. Dornte, R W , *Ind Eng Chem* , **28**, 26–30 (1936).
14. Dornte, R W , and Ferguson, C. V , *Ind. Eng. Chem.*, **28**, 863–6 (1936)
15. Dornte, R. W , Ferguson, C. V , and Haskins, C P., *Ind Eng. Chem.*, **28**, 1342–5 (1936).
16. Dupont, P., and Chavanne, G., *Bull. soc. chim Belg* , **42**, 537–43 (1933)
17. Exline, P G., Kramer, W E , and Bowman, J R , *J. Inst Petroleum*, **29**, 295–307 (1943)
18. Fenske, M R , Stevenson, C. E., Lawson, N. D., Herbolsheimer, G , and Koch E. F , *Ind. Eng. Chem* , **33**, 516–24 (1941)
19. Fenske, M R , Stevenson, C E , Rusk, R. A , Lawson, N D , Cannon, M R , and Koch, E F. *Ind Eng Chem* , *Anal Ed* , **13**, 51–60 (1941).
20. George, P , Rideal, E K , and Robertson, A., *Nature* **149**, 601–2 (1942)
20a. Georgi, C W , "Motor Oils and Engine Lubrication," p 177, New York, Reinhold Publishing Corp , 1950
20b. Gruse, W. A , and Stevens, D R , "The Chemical Technology of Petroleum," pp. 654–6, New York and London, McGraw-Hill, 1942.

21. Hanson, T. K , and Egerton, A. C., *Inst. Mech. Engrs.*, "General Discussion on Lubrication," Vol. II, pp. 334–40, 1937.
22. Haslam, R. T., and Frolich, P. K., *Ind. Eng. Chem.*, **19**, 292–6 (1927).
23. Hicks-Bruun, M. M , Ritz, B L., Ledley, R. E., and Bruun, J. H , *Ind. Eng. Chem.*, **36**, 562–8 (1944).
24. Hock, H., and Lang, S , *Ber.*, **75B**, 300–13, 1051–4 (1942).
24a Kalichevsky, V. A., *Petroleum Refiner*, **28**, 85–93 (1949).
25. King, E. O., *Proc. Roy. Soc. (London)*, **A139**, 447–59 (1933); *J. Inst. Petroleum Technol* , **20**, 97–114 (1934).
26. Larsen, R. G., and Armfield, F. A., *Ind. Eng. Chem* , **35**, 581–8 (1943).
27. Larsen, R. G., and coworkers, Shell Development Co., Unpublished work.
28. Larsen, R G., Thorpe, R. E., and Armfield, F. A., *Ind. Eng. Chem.*, **34**, 183–93 (1942)
29 Likhushin, K. P., Masumyan, V., and Levkupolo, N. *Azerbaĭdzhanskoe Neftyanoe Khoz*, **1934**, No. 10, 77–82, No 11–12, 87–9, *Chem. Abstracts*, **29**, 6034, 7629 (1935).
30. Moureu, C , and Dufraisse, C.; *Compt. rend* , **175**, 127–329 (1922); **176**, 624–9 (1923); *Compt. rend. soc. biol.*, **86**, 321–3 (1922); British patent 181,365 (1922).
31 Petrov, G S., *Trans VI Mendeleev Congr. Theoret. Applied Chem* , *1932*, **2**, Pt. I, 844–67 (1935); *Chem. Abstracts*, **30**, 3975 (1936)
32. Plisov, A. K , *Bull soc chim.* (*5*), **3**, 1274–81 (1936); *Chem. Abstracts*, **30**, 7829 (1936).
33. Plisov, A. K , Golendeev, V. P., and Zel'tsburg, A. I., *J Applied Chem. (U.S. S R.)*, **9**, 844–5 (1936); *Foreign Petroleum Technol.*, **4**, 237–43 (1936).
34. Plisov, A. K., and Grebennikova, M. D., *J. Gen Chem. (U S S R)*, **9**, 547–56 (1939); *Chem. Abstracts*, **33**, 9603 (1939).
35. Reiff, O. M., *Ind. Eng. Chem.*, **33**, 351–7 (1941).
36. Shoruigin, P. P., and Kreshkov, A P , *J. Gen. Chem. (U.S S.R.)*, **3**, 825–30 (1933); **4**, 988–94 (1934); *Chem Abstracts*, **28**, 6106 (1934), **29**, 2147 (1935).
37. Stevens, H. N , *J. Am. Chem. Soc.*, **48**, 1824–6, 2920–1 (1926), **50**, 2523–9 (1928).
38. Stevens, H. N., and Roduta, F. L , *J. Am. Chem. Soc.*, **57**, 2380–1 (1935).
39. Varlamov, V., *Masloboĭno-Zhirovoe Delo*, **1932**, No 4–5, 41–5, No. 6, 47–53; *Chem. Abstracts*, **27**, 3595, 5955 (1933)
40 Velikovskii, D. S., and Lemer, A. P., *Neftyanoe Khoz.*, **1937**, No. 2, 63–7; *Chem. Abstracts*, **32**, 4764 (1938).
41. Velikovskii, D. S , and Vasil'eva, O. V., *Neftyanoe Khoz* , **29**, No. 9, 62–7 (1935); *Foreign Petroleum Technol* , **4**, 209–35 (1935)
42 von Fuchs, G. H , and Diamond, H , *Ind. Eng. Chem.*, **34**, 927–37 (1942).

Chapter IV

BEARING CORROSION*

Introduction

Tin-base babbitt was used almost exclusively at one time as a bearing metal, and bearing corrosion was virtually unheard of, since this composition is very resistant to attack even by severely deteriorated lubricating oils. However, with the development of engines operating at higher speeds and loads, bearings became subjected to greater pressures and temperatures, and babbitt, which under more moderate conditions is an almost ideal bearing metal, began to fail due to inadequate fatigue resistance. This led to the development of new bearing compositions which are more durable mechanically, but which are generally more reactive chemically.

Bearing Metals

The following properties, in addition to such items as cost and availability, must be considered in the selection of a bearing metal for a given application:[6, 32, 33]

(1) *Fatigue strength.* The development of fatigue cracks which ultimately surround and undermine local areas, must be avoided. Fatigue is the most common cause of bearing failure in actual practice.[38]

(2) *Antifriction and nonscoring characteristics.* The coefficient of friction between bearing and shaft should be low, and the bearing and shaft should not seize during temporary periods of metal-to-metal contact. The bearing metal should have a low rate of wear, but should wear in preference to the shaft, since the latter is more difficult and costly to replace.

(3) *Bonding characteristics.* A strong bond between bearing metal and the steel or bronze back is essential.

(4) *Mechanical strength.* This is the resistance to extrusion by compression. Failures from this cause are not frequent, because most

* This chapter, which is based on a paper originally published in *Oil and Gas Journal*, Feb 16, Feb 23 and March 2, 1946, is used with the permission of the *Oil and Gas Journal.*

alloys contain hardening elements which raise the mechanical strength above the fatigue limit.

(5) *Conformability.* Bearings must adjust their dimensions to slight shaft deflections and misalignments.

(6) *Embeddability.* The bearing must embed small dirt particles and steel chips which find their way into the space between the bearing and shaft. Otherwise the shaft will be scratched or scored.

(7) *Corrosion resistance.* Corrosion, as mentioned earlier, has become a serious problem in the newer bearings containing cadmium or lead which were developed because of their greater fatigue resistance.

A large number of bearing metals have been developed, none of which possess all the above-mentioned properties in the optimum degree. All have their advantages and disadvantages. Since the relative importance of these requirements varies with the application, the choice of bearing metal varies likewise, and is often a matter of compromise.

Bearing metals can be classified into ten groups, largely according to composition. This classification is not absolute since there is considerable variation within most of the ten classes. Furthermore, some bearings are composed of two layers of bearing metal of different composition, i.e., the so-called "sandwich" bearing, which was used in the 1941 Buick.[46] However, practically all the bearings used today will fall into one of the following groups:

(1) *Tin-base babbitt.* A typical composition[89] consists of 89 per cent Sn, 7.5 per cent Sb, 3.5 per cent Cu. The journal box patented by Isaac Babbitt[2] in 1839 used an alloy of the general composition of pewter or Britannia metal, which belongs to this class. Tin-base babbitt is generally regarded as the best all-around bearing metal for conditions of moderate loads and temperatures. It has been used extensively in passenger cars, as shown in a survey of 1938 model cars.[1] All but three out of forty-six used babbitt in the main bearings, and all but five in the connecting rod bearings While the type of babbitt was not specified, it was probably tin-base in a majority of cases, since lead-base babbitt was not used to any great extent at that time.

(2) *Lead-base babbitt.* This type of bearing is somewhat inferior to tin-base babbitt,[6, 22] but has the advantage of lower cost and greater availability, particularly during periods of war. Five to ten

per cent of tin is often included, and the antimony content is roughly twice that of tin-base babbitt. About one per cent of arsenic is usually present.

3. *Alkali-hardened lead.* Lead is too soft to be used as a bearing metal by itself, but it can be hardened by the addition of a small amount of alkali or alkaline earth metal, e.g., Na, Li, Ca, Ba, Sr. A hard intermetallic compound is formed,[22] which is supported in the lead. This compound in the case of calcium in lead is Pb_3Ca, according to Brasch.[3] The amount of alkali or alkaline earth element present is normally of the order of one per cent. Bahnmetall, which contains calcium, lithium, and sodium, has been used in locomotives in Germany for a number of years, and Satco, which contains calcium, is used to a limited extent in this country, mostly in large bearings. Other members of this class are "No Heet", Ulco metal, Frary metal, Mathesius, and Lurgi Lagermetall.[25] Alkali-hardened lead is soft enough that it does not require specially hardened shafts. It is like babbitt in this respect. However, it does not have the corrosion resistance of babbitt.

(4) *Cadmium alloy.* Cadmium-silver, which was used in the 1935 Pontiac, consists of about 98 per cent cadmium, a small percentage of copper, and the remainder silver. Cadmium-nickel and cadmium-magnesium contain 0.25 to 7 per cent Ni, and 0.5 to 5 per cent Mg, respectively.[25] Cadmium alloy bearings have excellent mechanical properties, but are subject to corrosion, and are too hard to be used except with hardened shafts. Cadmium-silver requires a shaft having a minimum hardness of 250 Brinell.[38, 39]

(5) *Copper-lead.* This bearing metal is unique, according to Melhuish[22] and Raymond,[27] in that it consists of a hard copper matrix, with the softer lead particles interspersed. Both phases are probably continuous, since these bearings are sometimes made by sintering a mixture of the powdered metals This structure is different from that of most bearings, in which hard crystals are dispersed in a soft continuous supporting phase. The ratio of copper to lead varies from 25:75 to 50:50. The two metals are virtually insoluble in each other. Copper-lead bearings require a shaft having a minimum hardness of 300 Brinell. Like cadmium alloy bearings, they are subject to corrosion. They are used quite extensively in diesel engines.

(6) *Bronze.* Copper is the principal ingredient of this alloy. Tin is always present, and sometimes lead and phosphorus. Phosphor-

bronze is used in heavy-duty work, as in gearbox bushings and spring shackles; and lead-bronze, which contains up to 20 per cent lead, is used mainly in railroad engines. This type of bronze is used as a solid bearing, whereas the five classes mentioned previously are usually mounted on a steel or bronze back.

(7) *Silver*. Silver has many properties desirable in a heavy-duty bearing metal. It has good mechanical and fatigue strength, and resists corrosion, but its anti-friction characteristics are not entirely satisfactory. This property can, however, be improved by the incorporation of a low concentration of lead. Steel-backed silver bearings, plated with a thin deposit of lead, and then with a thin deposit of indium, are used in aircraft engines. They are said to have the advantages of silver, plus the requisite "oiliness", or antifriction characteristics, which pure silver lacks.[4]

(8) *Aluminum alloy*. Considerable work on aluminum bearings containing small amounts of copper, silicon, iron, or other metals, has been done in Germany.[19] Such bearings have good mechanical properties at high temperatures, good antifriction characteristics, low wear, and good thermal conductivity and workability. However, they have a high coefficient of thermal expansion which makes it difficult or impossible to bond the bearing metal to a steel shell, and necessitates special mechanical construction. They also possess poor run-in characteristics, due to their hardness and high melting points. An alloy containing approximately 90 per cent Al, with about 5 per cent Sn, 1 to 2 per cent Ni, and small amounts of other metals such as Cu, Mn, Si, Fe, Mg, and Sb, has been developed in England for use in aircraft engines. Bearings made from this alloy are said to resist corrosion. They require shafts in main bearings of at least 600 Brinell hardness, according to Hives and Smith.[16] However, Melhuish[22] claims that aluminum alloy containing a maximum of 0.4 per cent Si, and heat-treated at 180°C, can be used with crankshafts as soft as 280 Brinell, which is comparable to that required with copper-lead and cadmium-silver. Aluminum alloys have been studied in the United States, as well, and good performance is claimed for various compositions in diesel engine and other heavy-duty service.[14, 18] According to Hunsicker and Kempf,[18] an aluminum-tin-silicon-copper alloy, which contains 6.5, 2 5, and 1 per cent of tin, silicon, and copper, respectively, along with a small amount of nickel, is superior to previously developed aluminum alloys.

Magnesium alloys have also been investigated in Germany,[19] but they appear to offer no advantage over aluminum alloys.

(9) *Zinc alloy*. This is probably the least known of the ten groups in this classification. Melhuish[22] mentions an alloy containing 4 per cent Al, 2.7 per cent Cu, 0 03 per cent Mg, and the remainder zinc. It is inexpensive and can be die cast under pressure. It is used under conditions of mild loads and temperatures. Gersdorfer[12] sets the maximum temperature to which zinc alloys may be subjected at 70 to 80°C.

(10) *Sintered powdered metals*. These are generally made of powdered bronze which is placed in a mold and subjected to pressure and then sintered. They are usually impregnated with oil before use. Their principal application is in bearings which do not carry heavy loads, and which are difficultly accessible for lubrication. The "oilite" bearing is an example.

Relative Corrosion Resistance of Bearing Metals

As mentioned earlier, bearing metals differ widely in their resistance to corrosion. This is illustrated in Table 11, in which data published by Tichvinsky[31] are reproduced. The data are from Underwood tests*, in which oil is circulated at 325°F and impinged upon bearing specimens. Catalysis was supplied by means of copper baffles in the machine. Various S A E 30 grade oils were used Table 11 shows that the lead base babbitts are attacked to a greater extent than tin-base babbitt; however, all four babbitts were practically inert in comparison with the other four alloys. Copper-lead (coarse structure) and alkali-hardened lead were roughly equivalent in this test, with cadmium-silver more reactive by a factor of four, and cadmium-nickel by a factor of six. These factors are not regarded as absolute, since they vary with the oil used and with test conditions. Furthermore, the conditions of the Underwood test and engine operation differ markedly, However, a general trend is indicated in Table 11. Underwood tests conducted in the Shell laboratories at Emeryville and at Wood River have in general rated babbitt, copper-lead, and cadmium-silver in the order shown in Table 11.

These results are in agreement with the qualitative statement by Heldt[15] that cadmium is the least resistant to corrosion; high-lead bronze, copper-lead and alkali-hardened lead are moderately re-

* The Underwood and a number of other bearing corrosion tests are described briefly in Table 13.

TABLE 11. CORROSION OF VARIOUS BEARING METALS IN UNDERWOOD TEST AT 325°F IN PRESENCE OF METALLIC COPPER
Data from Tichvinsky[31]

Bearing Metal	Composition, Per Cent													No of Tests	Loss Grams/Hr
	Sn	Pb	Sb	Cu	Cd	Ag	Ca	Al	Zn	Mg	Fe	Ni	As		
Tin-base babbitt	88.0	0.35	7 5	4 0	—	—	—	—	—	—	0.03	—	0 1	17	0 001
Arsenic-lead base babbitt	1.0	82.5	15.0	0 5	—	—	—	—	—	—	—	—	1 0	13	002
Silver-lead base babbitt	2.0	77 75	15 0	25	—	5 0	—	—	—	—	—	—	—	4	.002
Lead-base babbitt	5.0	80 0	14 0	.3	—	—	—	—	—	—	—	—	0 2	7	004
Alkali-hardened lead	1 0	98 0	—	—	—	—	0 5	0.07	—	0.08	0 01	—	—	50	.427
Copper-lead, coarse structure	—	25.0	—	75.0	—	—	—	—	—	—	—	—	—	65	.453
Cadmium-silver	0 0	0.02	—	0 5	98 0	1.0	—	—	0 02	—	—	—	—	62	1 742
Cadmium-nickel	1	.01	0.18	04	97.8	—	—	—	—	—	—	1.8	—	4	2.424

sistant; and aluminum alloys, tin-base babbitt, lead-base babbitt of proper composition, cadmium-indium, low-lead bronze, and silver are practically inert.

Similar trends have been shown by Waters and Burnham,[37] who used the Existent Corrosivity, or EC, test, in which a test specimen is immersed in oil at 313°F for twenty minutes, during which time the oil is agitated by aeration at a fixed rate; and by Talley, Larsen, and Webb,[80] who used the Thrust Bearing Corrosion, or TBC, test, in which a bearing surface is subjected for 20 hours to a wiping

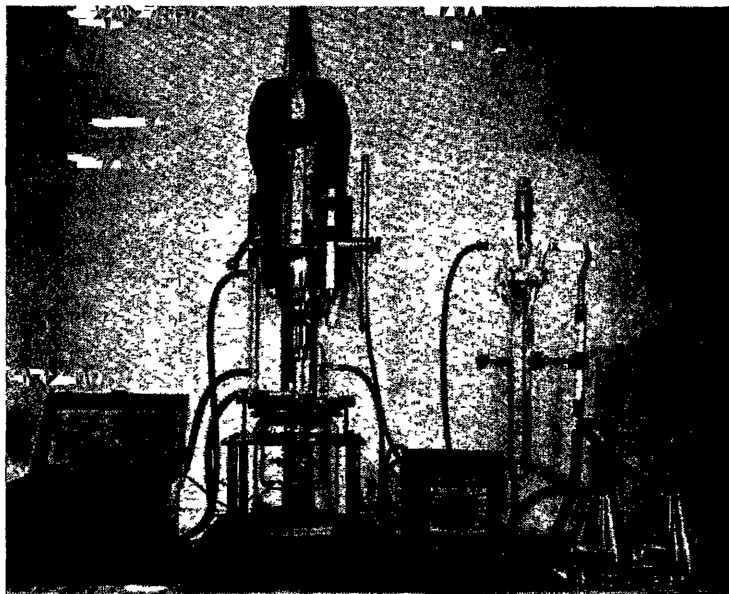


Figure 10 Corrosion and Stability Apparatus

action by steel at a pressure of 125 pounds per square inch and a temperature of 225°F. The results are summarized in Table 12. It will be observed that the babbitts were attacked to a negligible extent, with indium-plated copper-lead next in order, copper-lead next, and the cadmium alloys to the greatest extent.

The essential features of ten laboratory bearing corrosion tests, together with three engine tests, are summarized in Table 13 All these laboratory tests consist of exposing a specimen of bearing metal, prepared under specified conditions and weighed on an analytical balance, to the oil under test at a given set of conditions. Most

of these tests are made as fresh oils; however the conditions are such that oxidation takes place during the test. The only test listed in which virtually no oxidation takes place is the EC test, in which the specimen is exposed to a preoxidized oil for only a short time. The other tests are designed to provide a degree of oxidation comparable to that experienced in engine tests. Laboratory tests of this nature serve a very useful purpose in predicting the performance of crankcase oils in actual operation. They are relatively rapid and inexpensive in comparison to engine evaluations. However, none of them duplicate engine conditions (particularly with respect to the effect of the fuel). It is customary, therefore, to make preliminary studies in laboratory tests and then obtain confirmatory data in engines.

Raymond[27] compared various bearing metals in an engine test. His results on four alloys are summarized in Table 14. He found

TABLE 12 RELATIVE CORRODIBILITY OF DIFFERENT BEARINGS

Bearing Metal	Wt Loss in EC Test, mg/sq cm[a] (Data from Waters and Burnham[37])	Wt Loss in TBC Test, mg/sq cm[a] (Data from Talley, Larsen, & Webb[30])
Tin-base babbitt	0 06	0 20, 0 28
Lead-base babbitt	—	0 12, 0 41
Indium-plated copper lead	1 0 ± 0 1	— —
Copper-lead	1 4 ± 0 2	28 2, 28 7, 25 9, 28 9
Cadmium-nickel	1 65 ± 0 05	30 3, 36.5
Cadmium-silver	1.8 ± 0 0	31 1, 40 0

[a] An SAE 10 grade oil containing undecylic acid to a neutralization number of 2 0 was used in the EC measurements, and a corrosive reference oil in the TBC tests.

cadmium-silver to be most corroded, with indium-plated cadmium-silver, copper-lead, and alkali-hardened lead considerably more resistant to attack.

Raymond[27] investigated the effect of the structure of copper-lead upon its corrodibility. A regular coarse-structure alloy was compared with a special fine-structure alloy in a 100-hour test run in a diesel engine. The results are shown in Table 15. It will be observed that the fineness of structure is an important factor in corrosion The average weight loss for the eleven fine-structure shells was 1 365, which is less than the average figure of 4 363 for the coarse-structure shells by a factor of 3.2. The probable explanation is that the lead, which is corroded preferentially, is more readily accessible in the coarse- than in the fine-structure alloy. Fine-structure copper-lead is said to have superior mechanical strength as well as corrosion resistance.

As mentioned previously, bearing metals can be made less corrodible by covering the surface with another metal or alloy, e.g., the indium-plated cadmium-silver bearings discussed by Raymond, and the Buick sandwich bearing, which consists of a steel shell, covered with a layer of a sintered mixture of nickel and copper (40:60), which is in turn covered with a thin layer of babbitt.

The corrosion of cadmium-silver can also be prevented by the addition of a small amount of certain metals. Smart[29] found that cadmium alloys containing small amounts of zinc, tin, or indium were more resistant to corrosion than cadmium-silver or cadmium-nickel. Ryan[28] showed that the weight loss of cadmium-silver which was exposed to a used lubricating oil for 16 hours at 340°F was reduced from 24 to 13 mg by the addition of 0.1 per cent antimony to the alloy, and to 7 mg by the addition of 0.2 per cent. In view of these results it would appear that the corrosion resistance of lead-base babbitt may be due in part to its antimony content, which normally amounts to several per cent.

Since the relative corrodibility of bearing alloys is affected by test conditions, it is impossible to list the various alloys in order of their corrosion resistance without reservation. It may be stated, however, that under normal engine conditions coarse-structure copper-lead, alkali-hardened lead, and the cadmium alloys are in general the most easily corroded. Babbitt is quite inert to corrosion. Fine-structure copper-lead, and specially treated bearings such as indium-plated cadmium alloy, fall in an intermediate classification. Whether or not a given bearing corrodes depends upon a number of factors which will be discussed in a later section.

Mechanism of Corrosion

Bearing corrosion may be of three types: (1) "acid" corrosion, (2) "sulfur" corrosion, and (3) corrosion by aqueous acids.

"Acid" Corrosion. This type is by far the most prevalent, and involves solution by an acid of a metal which is relatively high in the electromotive series in much the same manner that metals like zinc and iron are corroded or dissolved by aqueous solutions of acids. The metals commonly occurring in bearing alloys which are affected most by this type of corrosion are cadmium and lead. There is a distinction, however, between corrosion by aqueous acids and acids present in lubricating oils in that the former can act as oxidizing agents toward metals above hydrogen in the electromotive

TABLE 13. BEARING CORROSION TESTS
Based on Table III of paper by Larsen[23]

Test	Reference	Test Conditions						Special Features and Comments
		Atmosphere	Rate of Circulation or Stirring	Oil Temp, °C	Time, Hr	Sample Size	Catalyst, in Addition to Bearings	
Caterpillar	Willey and Prutton, S.A E., White Sulfur Springs, 1940	Air	60 rpm	132	65	400 ml	None	Cd-Ag bearing segment used as stirrer
Sohio*	Burk *et al*, Petroleum Div. A.C.S, Atlantic City, Sept, 1941	Air Air	30 liters/hr	154 4	20, 65	160 ml	300 sq cm steel 20 sq cm copper	Catalyst area based on metals exposed in engine
Penn State	Hersh *et al*, *Refiner*, **22**, 197–205, July, 1943	Air	10 liters/hr	175	20, 50, 80	100 ml	8.25 sq in iron 15 75 in No 40 copper wire	Test Similar to Sohio—both are oxidation tests as well
Underwood	Mougey, S A.E. World Automotive Congress Preprints N.Y, 1939	Air	—	162 8	5, 10, 15	1500 ml	Copper or soluble metal naphthenates	Oil sprayed through air and impinged on bearing specimens
Stirring Ind.	Lamb *et al*, *Ind. Eng. Chem Anal. Ed.*, **13**, 317–21, 1941	Air	1300 rpm	165 6	72	250 ml	5 sq cm Cu 10 sq cm Fe	
MacCoull	MacCoull *et al.*, *S A.E. J*, **50**, 338–45, 1942	Air	3000 rpm	176 7	10	125 ml	Copper	Special sleeve bearing rotated about stationary steel shaft
C & S (Corrosion & Stab)	Waters *et al*, *Ind. Eng. Chem. Anal. Ed.*, **15**, 550–9, 1943	Air	1310 rpm	184	3, 5	225 g	None	Rotor serves as stirrer and bears felt pad which wipes bearing surface

E C (Existent Corrosivity)	Waters & Burnham, *Ind. Eng. Chem* , **36**, 263–71, 1944	Air	6 3 ml/min	156	0 33	20 g	None	Measures corrosivity of an oil in a given state—it is not a stability test
Sunbury	Matthews, *J. Inst Petroleum*, **35**, 436–53, 1949	Air	680 rpm	160	20 or more	400 ml	Copper	Bearing segment used as stirrer
T.B.C. Thrust Bearing Corrosion	Talley *et al* , Petroleum Div. A C S , Atlantic City, Sept , 1941	Air	2400 rpm 50 ml/min	Various	20		None	Bearing surface slides over steel surface, providing oil shear

* In a later paper (N Y A.C.S meeting, Sept., 1944) the Sohio test was revised as follows: Air flow increased to 70 liters/hr, temp reduced to 133 7°, time standardized at 36 hr, metallic iron and copper increased to 300 and 20 sq cm respectively, and soluble iron and lead added in the form of ferric 2-ethyl hexonate (012% as Fe_2O_3) and lead bromide (0 1%) The revised test is designed to correspond to the 36 hr Chevolet (L-4 test.

In addition to the above laboratory tests, the following engine tests, all of which have been standardized by the CRC, include an evaluation of bearing corrosion.

CRC Designation	Engine	Test Conditions				
		Load, BHP	Jacket Outlet Temp, °F	Oil Temp, °F	Speed, rpm	Test Duration, hr,
L-3-1143	4 Cylinder Caterpillar Diesel	37	200	212	1400	120
L-4-1143	Chevrolet	30	200	265 for 10 grade 280 for 30 grade and 50 grade	3150	36
L-5-1143	G.M Diesel, 3, 4, or 6 Cylinder	27 per cyl.	180	230	2000	50

series and dissolve these metals with the evolution of gaseous hydrogen. No other oxidizing agent is required. Oil solutions of organic acids, on the other hand, seem to attack metals like cadmium and lead only when another oxidizing agent is present. This oxidizing agent can act in a primary role in increasing the valence of the

TABLE 14 COMPARISON OF CONNECTING-ROD BEARINGS IN 8-CYLINDER PASSENGER CAR ENGINE AT 300°F BASE OIL TEMPERATURE
Data from Raymond[27]

Oil	Weight Loss, Grams/Whole Bearing			
	Regular Cd-Ag	In Plated		Alkali-hardened Pb
		Cd-Ag	Cu-Pb	
Oil F, Commercial Nonadditive	4.021 3.717	0.447	0 361	0 415
Oil F + Additive VI (Inhibitor)	0 179	.013	—	—
Oil J, Commercial, Detergent	4 995	2 323	—	—

TABLE 15. COMPARISON OF COARSE- AND FINE-STRUCTURE COPPER-LEAD BEARINGS
Data from Raymond[27]

Oil Temperature, 260°F

Oil	Weight Loss, Grams/Shell			
	Main Bearing[a]		Connecting Rod Bearing[b]	
	Coarse	Fine	Coarse	Fine
Oil A + Additive I, (inhibitor, detergent)	0.594	0 030	0 837	0 046
Oil A + Additive I, (higher concentration)	—	—	.383	.088
Oil B, Nonadditive	—	—	5 755	2 740
Oil B, + Additive I	4 595	0 153	—	—
Oil B + Additive III, (inhibitor)	—	—	1 650	1 037
Oil E + Additive I	8 077	2 186	3 518	0 268
Oil E + Additive IV, (inhibitor)	8 904	2 740	5 084	2 661
Oil C, Commercial Additive	—	—	8 596	3 061

[a] Lower shell only.
[b] Upper shell only.

metal, (e g., oxide formation) or in a secondary capacity in preventing polarization by free hydrogen through oxidation of the latter to water, or both.

Denison[9] has reported some work which indicates that peroxides act as oxidizing agents in the corrosion of bearing metals. He ob-

served that a lead test-strip suspended in an oil during oxidation became covered with an oxide coating in the early stages of oxidation when the peroxide content was high, but the acidity low. As oxidation proceeded, acids formed, and the oxide was dissolved. He also showed that an oil high in peroxides and low in acidity was more corrosive to cadmium-silver (in a test conducted in the absence of air) than one high in acidity but free of peroxides. A third sample which was high both in peroxide content and acidity was the most corrosive of the three. On the basis of these experiments, Denison suggests the following mechanism for corrosion in the case of highly refined oils:



$$M + AO_2 \rightarrow AO + MO$$
$$MO + 2HA \rightarrow MA_2 + H_2O$$

M = metal, AO_2 = peroxide, HA = organic acid, AO = ketone if it is assumed that AO_2 is a beta or higher hydroperoxide.

A paper by Prutton *et al.*[26] discusses the mechanism of the corrosion of cadmium and lead in some detail. The conclusions of these investigators are in agreement with those presented above. They found that lead and cadmium are not attacked by acids except in the presence of oxidizing agents such as molecular oxygen or peroxides. In the absence of acids peroxides were found to form an oxide film on the surface of the metal. In the presence of acids this film dissolves. They found that organic peroxides act as the oxidizing agent at high temperatures (above 100°C), and molecular oxygen at low temperatures This conclusion is quite consistent with the well-known observation that peroxides are seldom, if ever, found in appreciable concentration in used oils taken from engines This is because under engine conditions the peroxides act as oxidizing agents as fast as they are formed, and are themselves converted to other compounds. The decrease in importance of molecular oxygen with increasing temperature is probably associated with its decreasing solubility.

Davies[7] studied the corrosion of cadmium by organic acids in oil solution and confirmed the dependence of the rate of corrosion upon the presence of an oxidizing agent, in this case atmospheric oxygen. It might be expected that when cadmium is exposed to an oil which contains an organic acid and the system is exposed to air, the acid would become depleted as corrosion proceeds. The rate of corrosion

would then decrease. Davies showed, however, that the rate does not decrease with time but remains essentially constant. This rules out an earlier suggestion to prevent the corrosion of cadmium bearings by installing a "sacrificial" filter of cadmium plates in the oil line leading to the bearings.

"Sulfur" Corrosion. Silver and copper are characterized by a very strong affinity for sulfur as indicated by the solubility product constants of Ag_2S and CuS in water of only 1.6×10^{-49} and 8.5×10^{-45}, respectively. The sulfides of most metals are considerably more soluble than this. In view of the strong attraction between sulfur and the two above-mentioned metals, it is not surprising that sulfur corrosion of bearing metals is most serious in silver bearings and in the copper matrix of copper-lead. Corrosion of this type seems to be serious only under conditions of high temperature. The mechanism may be the formation first of a complex of bearing metal, e.g., copper, with a sulfur compound, which forms a passivating film on the bearing surface and is beneficial as long as it remains in that form. Under conditions of high temperature, however, the complex decomposes to form copper sulfide, which is hard and brittle, and which flakes off. This results in a loss of copper from the bearing, and may also lead to mechanical difficulty due to abrasion by the sulfide particles. Support for this theory is found in the behavior of the mercaptans occurring in raw transformer oil. These react readily with cuprous oxide to form cuprous mercaptide, which in turn decomposes to a molecule each of cuprous sulfide, mercaptan, and olefin. The mercaptan then reacts further with cuprous oxide, until ultimately all of the mercaptan sulfur is converted to a cuprous sulfide. The reaction rate is determined largely by the temperature. With a transformer oil containing approximately 0.1 per cent mercaptan sulfur, more than 10 hours was required to sweeten the oil at 400°F, but only 0.6 hours at 500°F.[36] von Fuchs[34] showed that the copper mercaptides of mercaptans occurring in gasoline decompose at temperatures above 350°F. Thus the temperatures occurring at a bearing surface may promote the reactions postulated above.

Corrosion by Aqueous Acids. This type of corrosion is like Type 2 in that copper is preferentially dissolved. It is not covered to any appreciable extent in the literature, but appears to be increasing in importance. Geniesse[11] has commented upon it, and associates it with low temperatures and insufficient venting. Similar comments

are made in a Bearing Manual issued by Clawson and Bals,[5] who attribute the preferential solution of copper to the presence of "fuel acids." These "fuel acids" may be organic acids of low molecular weight or sulfuric and sulfurous acid originating from sulfur in the gasoline. Since lead sulfite and sulfate are insoluble, it is quite conceivable that the latter acids would, in the presence of oxidizing agents, dissolve copper preferentially.

The mechanism of this type of corrosion is probably fundamentally similar to that of Type 1, the only major difference being the nature of the diluent.

Factors Influencing Corrosion

Corrosion, which is one of several possible causes of bearing failure, is in turn influenced by a number of factors. The effect of composition of the bearing, both chemical, as determined by analysis, and physical, such as grain structure and the presence of thin films of dissimilar metals, has already been discussed. Corrosion of a given bearing alloy is determined by the following factors: temperature; bearing load; venting; type of fuel; oxidation stability of lubricant; type of deterioration products formed in lubricant; dispersancy; passivation of bearing surface; action of sulfur; and presence of water.

The first four and the last are "engine"-, and the remaining five "oil"-factors. Certain of these factors are in a sense interrelated, but there is in all cases a clear-cut distinction.

Temperature. The temperature at the bearing-oil interface is determined by the temperature of the bulk oil and of the adjacent metal parts and rate of oil flow, which is in turn a function of the clearance between bearing and shaft. It is in general much higher than the bulk oil temperature.

Excessively high bearing temperatures are often associated with insufficient oil flow, caused by inadequacies in the design of the bearings or oil systems Pigott[25a] cited several examples of bearing failure which could be traced to design factors. The mechanism is usually one involving accelerated oxidation of the oil at the high temperature and corrosion by the oxidation products. In extreme cases the temperature may rise to a point where the bearing is damaged physically. Pigott observed, in the case of copper-lead bearings, loss of lead by sweating

Raymond[27] studied the effect of bulk oil temperature on bearing weight loss in a diesel engine operating with coarse-structure copper-lead bearings. His data are summarized in Table 16. It will be observed that corrosion was much more severe at the higher temperature, in spite of the shorter time. The average weight loss was 0.198 grams per 500 hours at the lower temperature, and 3.533 grams per 100 hours at the higher. If, for purposes of comparison, it is assumed that weight loss is a linear function of time, then the rate is 5 × 3.533/0.198, or 89, times as great at the higher temperature. Substitution in the Arrhenius equation shows that an 89-fold increase in rate per 30°F corresponds to a doubling in rate per 4.5°F (2.5° C)

TABLE 16 EFFECT OF TEMPERATURE ON BEARING WEIGHT LOSS IN DIESEL ENGINE USING CU-PB BEARINGS

Data from Raymond[27]

All Weight Losses in Grams per Bearing Shell

	Connecting Rod[a]		Main[b]	
Length of Run Bulk Oil Temp	500 Hours, 230°F	100 Hours, 260°F	500 Hours, 230°F	100 Hours, 260°F
Oil				
Oil A, Commercial, Nonadditive	0 091	0 270	0 066	1 031
Oil A + Additive I, (Inhibitor, Detergent)	505	837	203	0 594
Oil B, Nonadditive	355	5 755	244	4 861
Oil B + Additive III, (Inhibitor)	216	1 650	192	3 610
Oil C, Commercial Additive	050	1 596	.055	8 129

[a] Weight losses for upper shell only.
[b] Weight losses for lower shell only

increase in temperature, or a 16-fold increase per 10°C increase. This temperature coefficient is far greater than that normally encountered in oxidation studies, indicating that additional temperature effects are present. These may include a mechanical factor The hardness of bearing alloys decreases with temperature,[38] and any weight loss through abrasion would be expected to be more serious at the higher temperature The bearing temperatures may have been high enough to allow some loss of lead by sweating.[26a] Furthermore, in the case of the oils containing additives, there is a possibility that decomposition of the additives occurred at the higher temperature.

Davies[7] found, in plotting the rate of corrosion of cadmium against

temperature, that the curves invariably pass through sharp maxima at a temperature of about 160°C (320°F). Davies suggests that the low rate of corrosion at the high temperature may be caused by the instability of peroxides under these conditions.

Bearing Load. This factor is in general not critical. Variation in thrust from 15 to 125 pounds per square inch has comparatively little effect upon corrosion in the T.B.C. apparatus.[80] The small effect noticed was attributed to effect upon rate of shear, or removal of the products of corrosion.

Venting. Degree of venting can affect corrosion in two ways, and the two operate in opposite directions. With increased air flow, oxidation rate is increased, thus increasing the rate of formation of corrosive acids; however, the more volatile acids are removed by venting, so that the net effect may be one of increased or decreased corrosion, depending upon the relative importance of the two factors. The effect of crankcase ventilation upon bearing weight loss in a CFR engine equipped with copper-lead bearings has been studied by Griffith, Webb, and Hendricks[18] who found, with four different oils, that corrosion increases with increasing ventilation over the entire range studied (5 to 25 cu ft per hr). At 20 cu ft per hr the weight loss was two to three times the value for the same oil at a ventilation rate of 10 cu ft per hr. This indicated that the effect of increased rate of oxidation predominated. Davis,[8] on the other hand, found a marked decrease in the weight loss of cadmium-silver bearings with increased venting, both in the Underwood test and in a Pontiac engine The difference in trend in the two cases was quite striking. Several factors may be responsible for this difference. The engines used were different, although this does not appear to be an important factor here, since Davis found the same trend in the Underwood test and in the Pontiac engine. The most important point of difference, however, appears to be the type of bearings used; cadmium-silver in the one case, and copper-lead in the other. This would indicate the desirability, as far as bearing-corrosion is concerned, of maintaining crankcase ventilation at a maximum or minimum depending upon whether cadmium-silver or copper-lead bearings are being used.

These results can be explained by the theory that cadmium-silver is more readily corroded than copper-lead by the more volatile acids, while the reverse is true in the case of the heavier, nonvolatile

oxidation products. Support for this theory is found in work done by Hillman, Larsen, and Armfield[17] in which they measured the corrosion of both types of bearings by oxidized oils produced in their oxygen-absorption studies and by the volatile oxidation products collected in a cold-trap in the oxygen system. Their results are summarized in Table 17. It will be observed that, under the conditions used, the volatile acids were more corrosive to cadmium-silver than to copper-lead by an average factor of almost three, whereas the residual oil was more corrosive to copper-lead than to cadmium-silver by an average factor of about fifteen.

TABLE 17. CORROSION OF COPPER-LEAD AND CADMIUM-SILVER BY VARIOUS OILS AFTER OXIDATION AT 150°C

Data from Hillman, Larsen, and Armfield[17]

Oil	6-hr Test at 80°C on Volatile Oxidation Products		24-hr Test at 150°C on Residual Oxidized Oil	
	Cu-Pb	Cd-Ag	Cu-Pb	Cd-Ag
A	0.54	0.22	0.76	0 03
B	20	1.25	—	—
C	.92	1.60	97	.12
D	13	0.61	65	.03
E	45	1 30	.93	0
F	.08	0 67	.20	—
Average. .	39	94	69	05

Adequate venting, in addition to minimizing "acid" corrosion by volatile acids in oil solution, eliminates corrosion by aqueous acids, since it prevents the condensation of water in the crankcase.

Type of Fuel. Variation in fuels in internal combustion engines can have a pronounced influence upon bearing corrosion. The following factors may be involved with gasolines of varying composition: (1) acids produced by oxidation of the fuel may be corrosive; (2) the lacquer-depositing tendency of unstable fuels affects bearing corrosion, probably both directly, through the deposition of lacquer on the bearing surface, and indirectly, through passivation of the metal surfaces in the engine as a whole, thus reducing metal catalysis; (3) the decomposition products of tetraethyllead fluid in the fuel, lead to the formation of iron halides, which constitute the active portion of "crankcase catalyst;"[21] thus deterioration of the lubricant is more rapid when a leaded fuel is used; (4) lead soaps formed from

tetraethyllead may act as dispersants, thus making the metal surfaces more vulnerable to attack and resulting in increased catalysis by engine metals.

Oxidation Stability of Lubricant.* Fresh oils are in general only slightly, if at all, corrosive. They become corrosive primarily through oxidation, although decomposition products of additives and deterioration products of the fuel may act as corrosive agents. The stability of an oil is determined by a number of factors, particularly temperature, the availability of oxygen, and the presence of impurities or additives which may act as antioxidants, anticatalysts, or catalysts.

Type of Deterioration Products Formed in Lubricant. While oxidation stability is an important factor in bearing corrosion, it does not necessarily follow that oils of equal stability are equally corrosive, for the oxidation products may differ greatly in their effect on bearing metals. Products such as ketones, aldehydes, and esters

TABLE 18. EFFECT OF LACQUER FILM ON BEARING CORROSION
35 Hours in Chevrolet Engine Crankcase Temp. 275°F, Jacket Temp. 230°F
Data From Downing, Holbrook, and Fuller[10]

Test No.	Weight Loss of Copper-Lead Bearing, mg/sq in/1000 miles
1. Undoped oil, lacquered bearings, clean engine	3 98
2. Undoped oil, clean bearings, lacquered engine	34 38

probably have no effect, whereas acids and peroxides do. Even the acids themselves vary widely in their corrosive properties.

Dispersancy.† Excessive sludging and lacquering in an engine is highly objectionable, and has been overcome by the incorporation of peptizing agents or dispersants. The use of dispersants aggravates corrosion problems in that the surface of the bearings is left bare and vulnerable to attack by acids. The importance of lacquer films in protecting against corrosion is indicated in Table 18, which summarizes a portion of some work done by Downing *et al.*[10] on catalysis by engine metals. Tests 1 and 2 were identical except that in 1 the bearings were prelacquered in a four-hour run-in while the remainder of the engine was initially clean, whereas in Test 2 the bearings were clean and the other engine parts prelacquered. The large difference in weight loss shows the effectiveness of lacquer in protecting a bearing

* See Chapter III.
† See Chapter V.

surface against corrosion. If the other engine parts had been comparable in the two tests, the difference should have been even greater.

Passivation of Bearing Surface. Control of bearing corrosion in the presence of dispersants is difficult to achieve by the use of antioxidants alone, since the bearing surface is attacked in the presence of very low concentrations of acids in some cases. It is generally preferable to add a compound which is capable of laying down a protective film on the bearing surface. In the case of copper-lead bearings, sulfur compounds seem to act in this manner. The mechanism is probably that of the formation of a complex containing both copper and sulfur. These films are readily discernible by their dark color.

This does not mean that sulfur compounds act solely through this mechanism. Many undoubtedly act as antioxidants and deactivators for soluble catalysts as well, but passivation is in general their principal function.

Action of Sulfur. As indicated earlier, copper can be attacked preferentially in a copper-lead bearing by the action of sulfur at high temperatures. This highly undesirable condition, in which hard brittle particles of black material (probably copper sulfide) are broken off, probably differs from the formation of the desirable passivating films only in degree. As long as the film remains thin and adheres to the bearing surface it protects against acid corrosion, but when it becomes thick and begins to flake off, metal is lost through a "sulfur" type of corrosion. The sulfide particles may, furthermore provide an abrasive action.

Presence of Water. Water probably affects corrosion in several ways. Under anhydrous conditions acids tend to dehydrate to anhydrides, while in the presence of water they revert to the acid form, which is probably much more corrosive The presence of a separate water phase is, of course, necessary for the third type of corrosion mentioned earlier, namely, corrosion by aqueous acids. In addition, the presence of water has a pronounced effect upon rate of oxidation of an oil because of its effect on the rate of solution of catalytically active metals.[35]

Lead-base babbitt is readily corroded in oxidation tests conducted in the presence of water. This was clearly demonstrated in a cooperative A.S.T.M program in which Turbine Oil Stability Tests, in which the oil is oxidized in the presence of water, copper, and iron

at 95°C, were run on two oils in the presence of tin-base and lead-base babbitt.* The former bearing metal showed no appreciable weight loss, even when the oil was allowed to deteriorate somewhat beyond the end of its induction period, whereas the latter lost as much as several hundred milligrams per test specimen under identical conditions. The case of corrosion of lead-base babbitt is in marked contrast to its resistance to the conventional acid type of corrosion as shown in Table 11, this difference is attributed to the presence of water. The corrosion of cadmium alloys is also said to be greatly influenced by the presence of moisture.

Control of Corrosion

Miller[23] has listed the following four principal means of controlling bearing corrosion: (1) use of new bearing types, such as sandwich type, and indium-treated bearings; (2) operation of engines at lower temperatures; (3) selection and refining of crude used in the manufacture of the oil; (4) use of suitable inhibitors

The use of proper venting might be added to this list Of these five, only the third and fourth are "oil factors."

In the selection and treatment of crude, the proper choice will depend upon whether or not additives are to be used. If a mineral oil is to be used straight it should be selected and refined for maximum stability under conditions comparable to those to which it will be subjected in actual use, whereas an oil to be used as base stock for a compounded product should be chosen and refined for maximum susceptibility to the additives used. While considerable control over bearing corrosion can be exercised by the proper choice of stocks and treating method, the extent to which such control is possible is limited Engines which require the hard alloys as bearing metal are often operated under conditions which are severe for the oil as well as for the bearings The trend is, therefore, toward the incorporation of additives rather than relying solely upon the base stock. A large amount of work has been done on the development and testing of inhibitors for lubricating oils. Miller, Winning, and Kunc[24] listed 105 patents on antioxidants and metal passivators in 1940. Since that time many more patents have been granted in

* The babbitt used in this work contained about 1 per cent tin. There have been indications that lead-base babbitt containing 5 per cent tin is much more resistant to this type of corrosion.

this field, as indicated in a paper by Wright,[41] published in 1945, which lists 662 United States patents on antioxidants for lubricating oils.

As mentioned earlier, it is very difficult to distinguish between antioxidants and corrosion inhibitors since oxidation and bearing corrosion are generally interrelated. Most of the compounds mentioned in Chapter III as commercially used antioxidants may be regarded as corrosion inhibitors. Some of these act in this capacity directly, through the formation of protective films, and others indirectly, through their effect upon the over-all rate of oxidation. Phosphorus and sulfur derivatives are more likely to act by the former mechanism, and phenolic and amine compounds by the latter.

Bibliography

1. *Automotive Inds.*, 562, Oct. 23, 1937.
2. Babbitt, I., U. S. Patent 1,252 (1839).
3. Brasch, W., *Tech. Zentr. prakt Metallbearbeit.*, **46**, 452–8 (1936).
4. Bregman, A., *Iron Age*, 65–7, Aug. 13, 42–5, Aug. 20 (1942).
5. Clawson and Bals, Inc., "Engine Bearing Manual," Chicago, 1944.
6. Corse, W. M., "Bearing Metals and Bearings," New York, Chemical Catalog Co , Inc., (Reinhold Publishing Corp.), 1930.
7. Davies, C. B., *Trans. Faraday Soc.*, **42**, 305–16 (1946).
8. Davis, L. L., Paper presented before A S.T.M., Committee D-2, Atlantic City, June, 1938.
9. Denison, G. H , *Ind. Eng. Chem.*, **36**, 477–82 (1944).
10 Downing, F. B., Holbrook, G. E., and Fuller, J. H , Am. Chem Soc , Petroleum Div. Preprints, Baltimore meeting, April, 1939.
11. Geniesse, J. C , Paper presented before A.S.T.M , Committee D-2, Atlantic City, June, 1942.
12. Gersdorfer, O , *Metallwirtschaft*, **21**, 563–4 (1942)
13. Griffith, L. W., Webb, J. L., and Hendricks, H. R., Shell Oil Co., Wood River Research Laboratory, unpublished work.
14. Grim, G. B , *Automotive and Aviation Inds.*, **95**, 28, 29, 86, Nov. 1, 1946
15 Heldt, P M , *Automotive and Aviation Inds.*, **96**, 28–31, 58, 60, March 1, 34–7, 62, April 1, 1947.
16. Hives, E. W., and Smith, F. L , *S A.E Journal*, **46**, 106–17 (1940).
17. Hillman, E. S , Larsen, R. G., and Armfield, F. A , Shell Development Co., unpublished work.
18 Hunsicker, H. Y , and Kempf, L. W., *S A E Quart. Trans* , **1**, 6–27 (1947).
19 Kuhnel, R., "Werkstoffe fur Gleitlager," Berlin, 1939; Reproduced by Edwards Bros., Ann Arbor, Michigan, 1943
20 Larsen, R. G , Am. Chem. Soc , Petroleum Div. Preprints, New York meeting, Sept , 1944.
21. Larsen, R. G , and Armfield, F. A., *Ind Eng. Chem.*, **35**, 581–8 (1943)
22. Melhuish, M , *J. Inst Automobile Engrs* , **9**, 1–12 (1940).

23 Miller, F. L., *S.A E. Journal*, **45,** 290 (1939).
24 Miller, F. L., Winning, W. C., and Kunc, J. F , Am. Chem. Soc., Petroleum Div. Preprints, Detroit meeting, Sept., 1940.
25. Mougey, H. C., *Ind. Eng. Chem., News Ed.*, **14,** 425–8 (1936)
25a. Pigott, R. J. S., *S.A.E. Journal*, **48,** 165–73 (1941).
26. Prutton, C. F., Frey, D. R., Turnbull, D , and Dlouhy, G , *Ind. Eng. Chem.*, **37,** 90–100 (1945).
27. Raymond, L , *S A.E. Journal*, **50,** 533–7 (1942).
28. Ryan, J. G , U S Patents 2,116,851 and 2,136,655 (1938).
29. Smart, C. F., *Trans. Am. Soc. Mech. Engrs.*, **128,** 295–307 (1938).
30. Talley, S. K , Larsen, R. G., and Webb, W. A., Am. Chem. Soc., Petroleum Div. Preprints, Atlantic City meeting, Sept., 1941.
31. Tichvinsky, L. M., *S.A.E. Journal*, **51,** 69–77 (1943).
32. Underwood, A. F., "A.S.T.M Symposium on Lubricants," pp 29–52, 1937.
33. Underwood, A. F., *S.A.E. Journal*, **46,** 99 (1940).
34. von Fuchs, G. H., *Petroleum Z.*, No. 11, 5–8 (1933).
35. von Fuchs, G. H., Wilson, N. B , and Edlund, K. R., *Ind. Eng. Chem.*, Anal. Ed. **13,** 306–12 (1941).
36. von Fuchs, G. H., and Zuidema, H. H , U. S. Patent 2,276,526 (1942).
37. Waters, G. W., and Burnham, H. D., *Ind. Eng. Chem.*, **36,** 263–71 (1944).
38. Watson, R. A., *S.A.E. Journal*, **48,** 41–50 (1941).
39. Willi, A. B., *S.A.E. Journal*, **45,** 513–25 (1939).
40. Wolf, H. R., *S.A.E. Journal*, **48,** 128–37 (1941).
41. Wright, W. A , *Natl. Petroleum News*, Tech. Sect , R34-7 (1945).

Chapter V

SLUDGE AND LACQUER DEPOSITION*

Introduction

As mentioned in Chapter III, the oxidation of a lubricating oil often leads to the formation of oil-insoluble products. These products are sometimes found as particles which settle from the oil in the form of sludge, and sometimes as lacquer or varnish-like coatings on the engine parts. They frequently contain extraneous material, particularly in the case of deposits formed in internal combustion engines. Contaminants such as dust, water, products of incomplete combustion of the fuel, iron oxide resulting from wear of the engine, and lead oxides or salts resulting from the combustion of leaded gasolines often play a major role in the formation of engine deposits. The relative importance of the oil and extraneous factors depends largely upon the operating conditions of the engine.

Lacquer deposits may vary in intensity from thin coatings which are quite innocuous and which may be beneficial as protective films to heavy deposits which are capable of sticking valves, rings, or tappets, and which in extreme cases stick engines so that they cannot be operated. Instances have been reported in which pistons and tappets were stuck permanently and could not be removed without damage to the parts.[15] Lacquer deposition in the piston ring belt area is of particular concern in diesel engines. Sludges may likewise vary from harmless light deposits which settle out or which are removed by filters to large particles of "coffee ground" sludge which have been known to plug oil lines and eventually cause bearing failure through lack of lubrication.[19] Sludge formation is often a problem in spark-ignition engines.

Mougey[20] has classified the formation of sludge and lacquer or varnish as follows:

(1) Low Temperature
(2) Intermediate Temperature
(3) High Temperature

* This chapter, which is based on a paper originally published in *Oil and Gas Journal*, Jan. 8, 15, and 22, 1948, is used with the permission of the *Oil and Gas Journal*.

This is practically identical to an earlier classification for crankcase deposits proposed by Gruse and Livingstone:[13]

(1) Winter Sludges—Emulsions
(2) Intermediate Temperature Sludges
(3) High Temperature Sludges—Asphaltenes

Low temperature sludge, or "mayonnaise sludge", is generally associated with intermittent operation under light load at low ambient temperatures. Water invariably collects in the crankcase under such conditions and forms an emulsion. There is usually a sufficient concentration of polar compounds or suspended solids present in used crankcase oils to stabilize such an emulsion, which may block oil lines and screens and cause burned-out bearings and scored cylinders.[13] Control of low temperature sludge is largely a matter of engine design and operating conditions. There is little that can be done to the fuel or lubricant to prevent sludging if the operation is such that water collects in the oil. If, on the other hand, the operating temperatures are raised by the use of suitable thermostats and if adequate ventilation is provided, no difficulties of this nature are encountered.

Both diesel and spark-ignition engines are often run under conditions which fall in the moderate temperature range. The fuel, rather than the lubricant, is usually the major source of sludge and lacquer formed under these conditions. Two of the most commonly used engine tests for evaluating the performance of engine oils under moderate temperature conditions are the L-1[7] and the FL-2.[1, 2, 4] Both are run on dynamometer test stands, the former in a single cylinder Caterpillar diesel engine, and the latter in a regular Chevrolet engine. The test consists in each case of running the engine under a set of carefully controlled conditions and examining the engine parts for sludge and lacquer at the conclusion of the test

In high temperature operation the fuel may still play a part in the formation of deposits, but the conditions are sufficiently severe so that deterioration of the oil is an important factor. The engine test that is probably the most widely used for studying high temperature engine performance is the L-4 test.[7] It, like the FL-2, is run in a Chevrolet engine, but the conditions are quite different, as shown in Table 19.

While full-scale engines are commonly used in testing lubricants, small single cylinder installations are often preferable, particularly for screening work, because of their lower cost, greater simplicity,

and lower sample requirement. Single cylinder Lauson engines have been used quite extensively for this purpose, particularly in the case of high temperature work. Georgi[10] has reported cooperative test results from nineteen laboratories. The test conditions used in that work varied to a considerable extent. Speed varied from 1200 to 1800

TABLE 19. OPERATING CONDITIONS USED IN CHEVROLET ENGINE TESTS

	L-4*	FL-2†
Test duration, hours	36	40
Engine speed, rpm	3150	2500
Brake load, hp	30	45
Oil temperature, °F	265, 280‡	155
Jacket inlet, °F	190	85
Jacket outlet, °F.	200	95

* Taken from CRC Handbook[7], p 397–8.
† Taken from Albright et al [1]
‡ SAE 10 oils are tested at 265°F; SAE 30 and 50 at 280°F

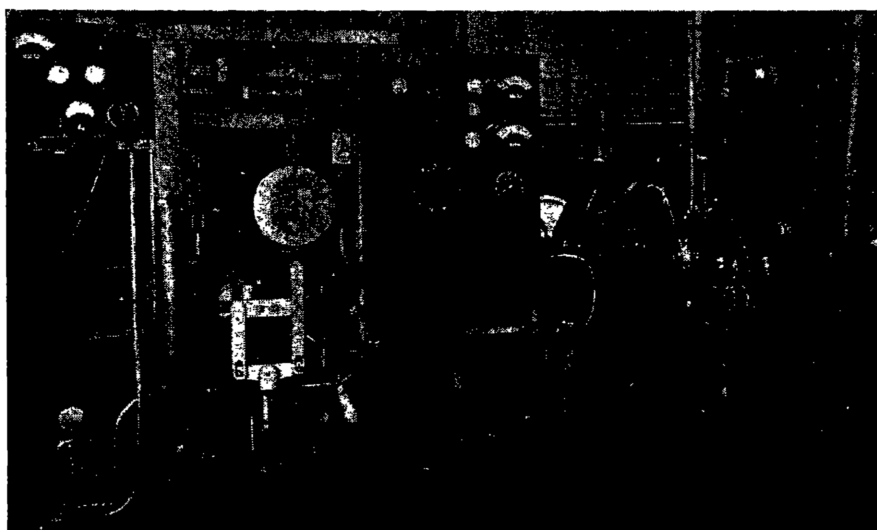


Figure 11. Full-scale Automotive Engine on Test Stand.

rpm; load from 1 to 3 hp, oil temperature from 212 to 320°F; jacket temperature from 170 to 400°F; and the duration of the test from 24 to 144 hours. On the basis of these cooperative tests on six oils it was concluded that oil temperature, jacket temperature, and the duration of the test are the most important factors. Engine speed and load were found to be less critical. Georgi tabulated three sets

of operating conditions which represent general averages of the conditions used by those laboratories which reported the most consistent results on the six oils. These are given in Table 20.

Conditions A and B differ only in temperature. The former includes a relatively high oil temperature and relatively low jacket temperature, whereas the latter has a lower oil temperature but a much higher jacket temperature. Procedure C differs from B only in that the jacket temperature has been raised an additional 50 to 55°F and the duration of the test reduced.

Forty-hour Lauson tests have been used for some time at the Research Laboratories of the Shell Oil Company at Wood River for studying lacquer deposition on piston skirts and connecting rods. Oil temperature and jacket temperature of 285°F and 212°F, respectively, are normally employed. At the completion of the test

TABLE 20. AVERAGE TEST CONDITIONS FOR LAUSON ENGINE
Taken from Georgi[10]

	A	B	C
Oil temperature, °F	280	225	225
Coolant temperature, °F	180–200	345–350	400
Test time, hours	100–120	100–120	24–48
Engine speed, rpm	1600–1800	1600–1800	1600–1800
Load, hp	1 3–1 6	1.3–1.6	1 3–1.6

the engine is disassembled and the piston and connecting rod rated according to the following "point score" system:

No lacquer	10
Light and transparent deposit	8
Light deposit, straw to tan in color	6
Medium deposit, golden brown	4
Medium heavy deposit, red-brown to deep brown	2
Very heavy deposit, dark brown to black	0

An average is taken for ratings at seven different areas. These include the following:

Piston skirt
- (1) Thrust side
- (2) Anti-thrust side
- (3) Pin hole regions

Underside of Piston
- (1) Crown
- (2) Piston skirt and pin bosses

Connecting Rod
(1) Big end bearing region
(2) Recessed sections of rod

There are a number of factors which influence sludging and lacquering in an engine. These are discussed in the following two sections, the first of which takes up the formation and the second the deposition of oil-insolubles

Factors Influencing Formation of Oil-insolubles in an Engine

Composition of Fuel. While the problem of lacquer formation in engines was originally thought of as involving solely lubricating oils, it has been known for some time that the composition of the fuel may be an important factor. This is true both in diesel and in spark ignition engines. Bouman[3] pointed out as early as 1933 that lacquer formation on the pistons, cylinder liners, etc., in diesel and hot-bulb engines is due to the incomplete combustion of the fuel at low loads, and not the lubricating oil. Cloud and Blackwood[6] studied the effect of various fuels upon deposition in high speed diesel engines, and concluded that sulfur content is the most important factor. Other properties which influence deposition include ignition quality, viscosity, and/or volatility.

The possibility that gasoline gum accumulating from diluent in the crankcase oil may be a factor in the formation of lacquer was pointed out by Gruse and Livingstone[14] in 1939. The importance of the gasoline in determining lacquering tendencies in spark ignition engines is now generally recognized. Mougey[20] has shown, as far as lacquering and sludging are concerned, that the fuel is of particular relative importance in engines operating at moderate temperatures. At high temperatures the oil rather than the fuel is primarily responsible for lacquering and sludging.

The influence of the composition of the fuel upon lacquering in the Lauson engine under a given set of high temperature operating conditions is demonstrated in Table 21. It will be observed that fuel B, which was a commercial cracked gasoline, gave a lacquer rating 2 2 to 2.4 units lower than fuel A, which consisted of straight run components normally used in aviation gasoline, when both were run with the same lubricant. While this effect is appreciable, it is not nearly so great as that obtained in tests conducted at lower temperatures (FL-2). Bowhay and Koenig[4] found, for example, in comparing

a special cut from aviation gasoline production with a regular motor gasoline that the former gave only 14 per cent the quantity of deposits on piston skirts, oil rings, oil pan, and cover plates as the latter.

Composition of Lubricating Oil. The basic oxidation stability and inhibitor susceptibility of an oil are determined by the composition of the oil. The presence of comparatively low concentrations of certain impurities is highly detrimental in this regard. The composition of the oil also determines to a large degree the type of oxidation product formed. Oils high in aromatics and sulfur form more insoluble oxidation products. This is particularly true of highly polar aromatics having a condensed ring structure, in contrast to the less polar aromatics remaining in an oil after solvent extraction. It has been shown[28] that the tendency of a California distillate to produce asphaltenes upon oxidation decreases markedly with increasing degrees of extraction. More direct evidence with respect to the effect of aromatics on lacquer formation is shown in Figure 12, where lacquer rating is plotted against per cent of unextracted oil in a blend with a Duo-Sol extracted stock. These two components had specific dispersion values of 143 9 and 107.3, and VI values of 41 and 97, respectively. It will be observed that the presence of a comparatively low concentration of the unextracted stock in the blend had a profound effect on lacquering tendency, both in the Lauson and Chevrolet engine. This effect cannot be explained by differences in over-all stability, and must be attributed to differences in the nature of the oxidation products. Another example is the relative behavior of white oil and the SAE-10 oil, shown in Table 21, in the Lauson test with a straight run gasoline as fuel. The former gives a lacquer rating of about 9, and the latter about 5; although the former is by far the less stable of the two it produces much less lacquer, for its oxidation products, which are nonaromatic, are almost completely soluble or volatile, while an appreciable portion of oxidation products of the latter are insoluble.

Various additives affect the formation of oil insolubles; some are beneficial in this respect and others are detrimental. Antioxidants and anticatalysts (deactivators and passivators) decrease the rate of formation of oil insolubles through their effect upon overall rate of oxidation. Certain additives, however, form oil-insoluble deterioration products, and thus contribute directly toward the formation of potential lacquer, even though they may inhibit oxidation of the

oil. Phenyl-α-naphthylamine is an example of this type of additive. Although it appears off-hand to be paradoxical, dispersants in general tend to increase the rate of formation of oil-insolubles in an engine. This is due to their ability to keep engine surfaces clean and

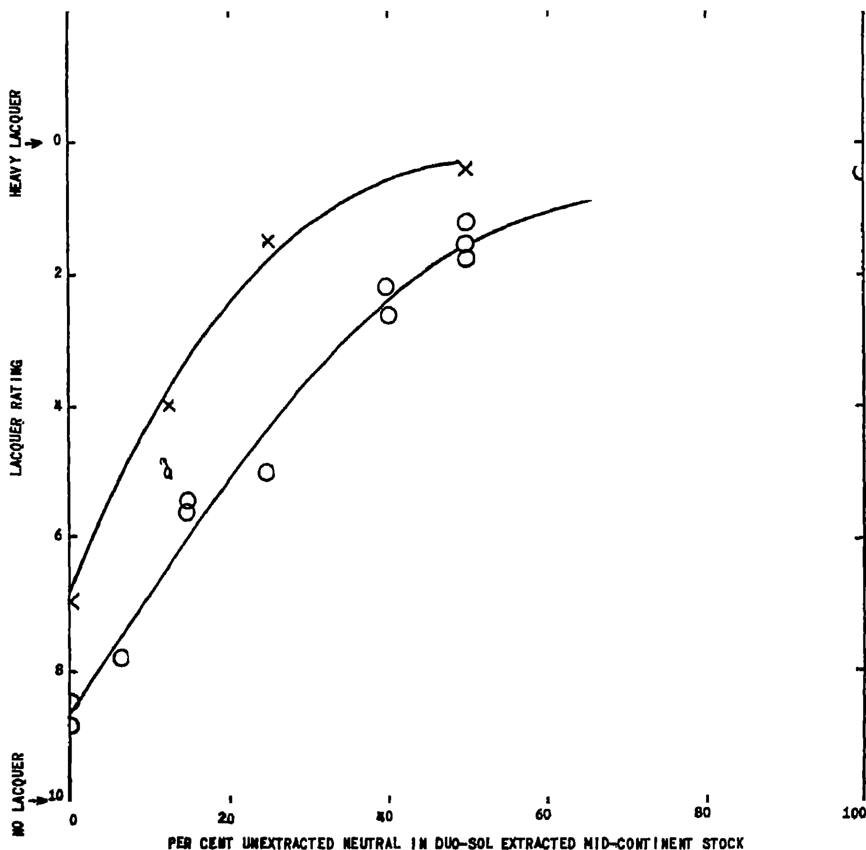


Figure 12. Effect of Oil Composition on Lacquer Rating (Unleaded Aviation Gasoline Used as Fuel)
× Chevrolet Engine ○ Lauson Engine

vulnerable to attack by acidic oxidation products, thus enhancing metal catalysis. As far as lacquer formation is concerned this effect is, of course, more than offset by the beneficial effect of the dispersant in preventing deposition, as will be seen in the next section, but it does constitute a problem with respect to over-all oxidation and bearing corrosion.[28, 29]

Conditions. The conditions under which an engine is operated have a profound effect upon the rate of formation of oil-insolubles, both from the oil and from the fuel. As mentioned previously, temperature is one of the most important conditions as far as effect upon the formation of deposits is concerned.

The effect of temperature upon the formation of oil-insolubles from the oil can be explained by the well-known exponential rela-

TABLE 21. EFFECT OF FUEL AND LUBRICANT ON LACQUER RATING
(40-hr Lauson Tests. Oil Temp. 285°F, Jacket, 212°F)

Lubricant	Gasoline	Average Lacquer Rating*
1. White Oil	A	8.9 (9.2, 8 7)
White Oil	B	6.7 (7.5, 6.2)
2. Duo-Sol Extracted SAE-10	A	8 8
Duo-Sol Extracted SAE-10	B	6.4
3. Duo-Sol Extracted SAE-10	A	4.9 (5.3, 4.6)
Duo-Sol Extracted SAE-10	B	2 5 (2.9, 2 4)
Change in lacquer rating with change in Fuel, Lubricant 1		2 2
Change in lacquer rating with change in Fuel, Lubricant 2		2.4
Change in lacquer rating with change in Fuel, Lubricant 3		2 4
Change in lacquer rating with change in Lubricant, 1 to 2, Fuel 1		0.1
Change in lacquer rating with change in Lubricant, 1 to 2, Fuel 2		.3
Change in lacquer rating with change in Lubricant, 1 to 3, Fuel 1		4 0
Change in lacquer rating with change in Lubricant, 1 to 3, Fuel 2		4 2
Change in lacquer rating with change in Lubricant, 2 to 3, Fuel 1		3 9
Change in lacquer rating with change in Lubricant, 2 to 3, Fuel 2		3.9

* Scale defined on page 103.

tionship between temperature and rate of oxidation. From this standpoint low operating temperatures are desirable.

The influence of temperature upon the formation of oil-insolubles derived from the fuel is more complex. At low temperatures there may be more oxidation of fuel components to oil-insolubles, since there is a higher concentration of fuel dilution present in the oil under low temperature conditions and since the fuel is normally much less resistant to oxidation than is the lubricant. At high temperatures the diluents in the lubricating oil are vaporized and removed from the crankcase. It has been pointed out by Mougey[20]

that heavy piston deposits are built up in the FL-2 test when certain fuels are used in conjunction with either straight mineral oils or heavy-duty lubricants One such fuel was shown to give excellent results when run with a heavy-duty oil in the L-4 test, which differs from the FL-2 test primarily in that much higher jacket and oil temperatures are used (see Table 19).

Bowhay and Koenig[4] have shown the effect of several factors upon the deposition of "low temperature sludge" upon piston skirts, oil rings, and the oil pan and cover plates. An increase in jacket temperature from 95 to 120°F had a marked effect in reducing deposition, and a further increase to 180°F had a further effect in the same direction. This, of course, constitutes a strong argument in favor of high-temperature thermostats in the cooling systems of engines. Marked reduction in deposition was also brought about by raising the intake manifold temperature from 95 to 190°F. Here, as in the case of jacket temperature, the increase in temperature probably reduced the quantity of fuel present in the liquid state, and hence resulted in less dilution of the oil, thereby decreasing the concentration of "potential deposits" in the oil.

Thus the optimum temperature in an engine, as far as obtaining freedom from lacquer and sludge deposits is concerned, is a matter of compromise. Too low a temperature results in excessive deposits derived from the fuel and too high a temperature results in excessive oxidation of the oil. However, since present oils are made to resist oxidation at fairly high temperatures, operation at moderately high temperatures is to be preferred

Catalysis by engine metals, particularly copper and iron, and by "crankcase catalyst", which has as its main active ingredients iron halides formed from the engine metal and halogens occurring in tetraethyllead fluid, is another important factor in determining the rate of formation of engine deposits

The presence of water in the crankcase may have a pronounced effect upon rate of oxidation of the oil, although this factor does not appear to have received much study. Water is, however, known to have a marked effect upon the length of the induction period of a turbine oil in the Turbine Oil Stability Test,[25] which is run in the presence of metallic copper and iron An oil which had an induction period of only 110 hours in the standard test with water present lasted for more than 400 hours in the absence of water. Similar re-

sults have been observed in an accelerated bomb test run in the presence of oxygen and the same two metals used in the above-mentioned test. The presence of water decreased the "life" of various oils by a factor of 3 to 10. This effect is probably associated with metal catalysis.

The presence of water, like that of dilution, in an engine can be controlled through the control of temperature. Crankcase ventilation is another important factor which influences the amount of water and dilution present.[18] Without effective ventilation the advantages of optimum operating temperatures are not fully realized.

Factors Influencing Deposition of Oil-insolubles in an Engine

Hydrocarbon Composition of Lubricating Oil. While the composition of an oil affects lacquer primarily through its effect upon the formation of oil-insolubles, there is an additional effect upon deposition. This is illustrated in Figure 13, in which each point represents an experiment in which a given weight of asphaltenes in benzene solution was added to an oil, after which the solution was heated under specified conditions and filtered to determine the extent of peptization and solution of asphaltenes It will be observed that the presence of diamyl anthracene had a pronounced effect, whereas that of mono-, di-, and polyamyl naphthalene had much less effect upon the ability of the oil to dissolve or peptize asphaltenes. White oils differ appreciably in this respect depending upon their naphthene content, as shown in the third curve in Figure 13.

These results indicate that paraffins have poorer solvent and/or antiflocculant properties than naphthenes and aromatics. Since a high Viscosity Index is associated with a high paraffin content it follows that oils of high Viscosity Index are at a disadvantage with respect to holding asphaltenes in solution or colloidal dispersion. The use of base stocks of high Viscosity Index thus imposes more of a burden upon the added dispersant.

Dispersants. Straight mineral oils are deficient in their ability to prevent deposition of lacquer and sludge under severe operating conditions, and it is general practice to correct this condition, particularly in heavy duty oils, by the incorporation of specific addition agents. Such oils are commonly known as "detergent" oils, and the additives responsible for this function are usually referred to as "detergents." These terms are misleading, since the adjective "de-

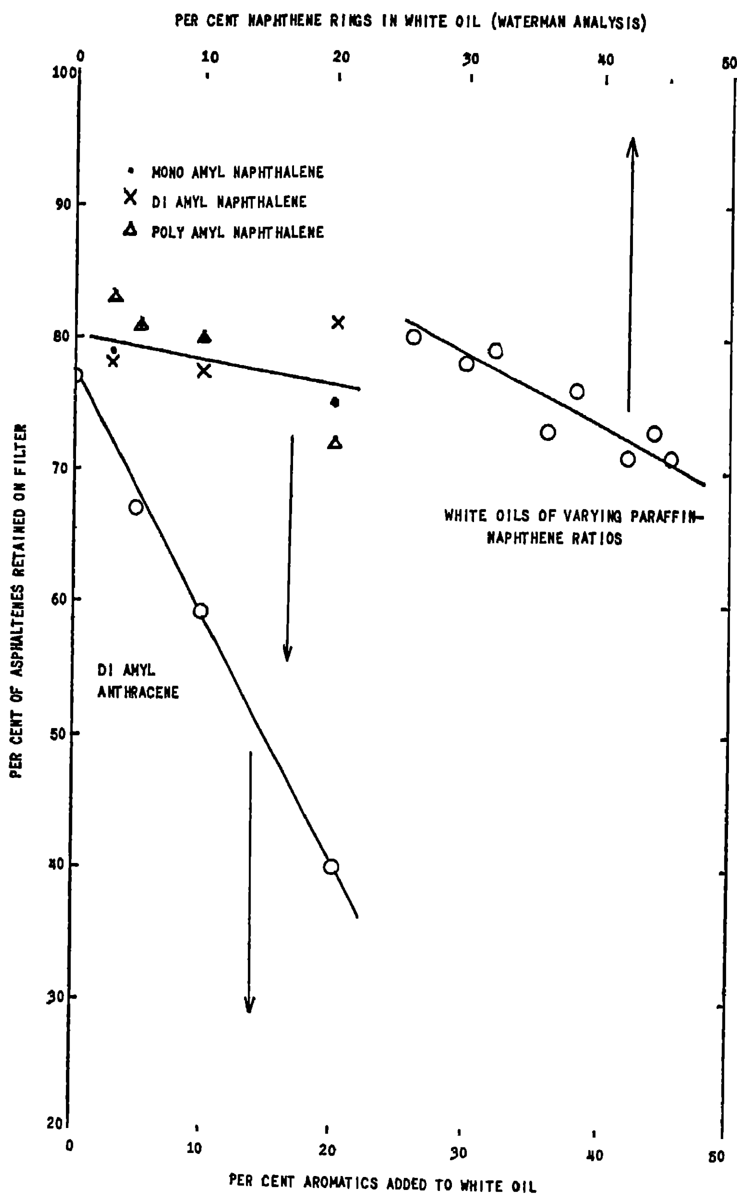
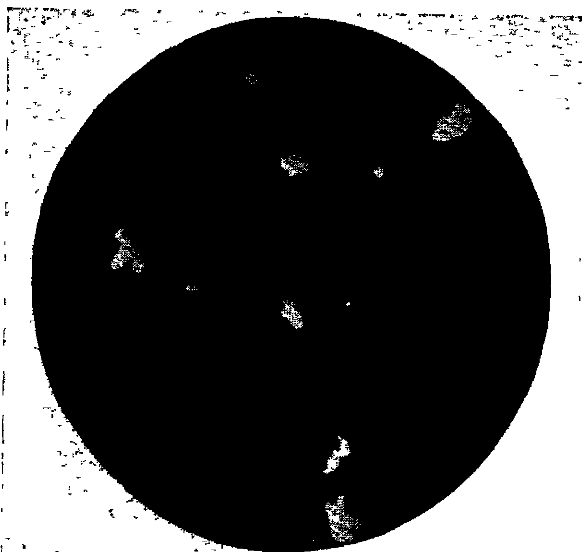
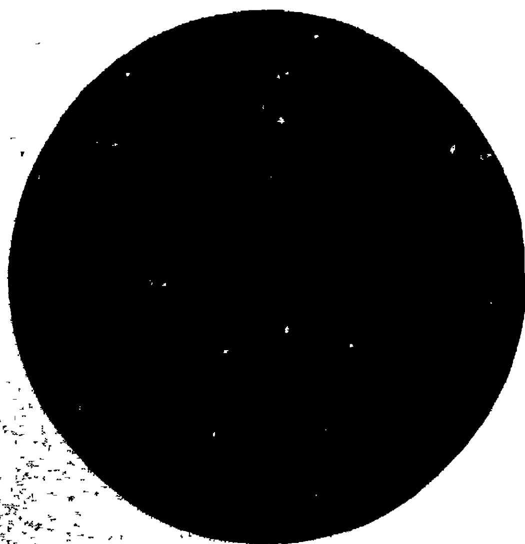


Figure 13. Effect of Hydrocarbon Composition upon Solvent and Antiflocculant Properties of Oil

tergent" means "cleansing" or "purging", while the function of the additives in question is primarily that of preventing deposition rather than that of removing deposits formed previously. Georgi[11] has suggested the term "dispersant" as being more descriptive. The term "antiflocculant" expresses the function quite accurately and would, therefore, be used here except for the fact that the use of "dispersant" has already been established. Dispersants are defined as additives which prevent the flocculation or coagulation of colloidal particles. It should be understood that flocculation can occur either within the interior of the oil phase, with a resulting precipitation of large sludge particles, or on engine surfaces in the form of a resin or lacquer. A dispersant may have detergent properties, but if it is added to a fresh oil which is placed in a clean engine it need function only as an antiflocculant, for the insoluble materials pass through the colloidal state in the process of their formation, and the additive needs only to maintain the system in that state However, it may exhibit some detergent properties if added to an engine containing deposits formed previously. Several of the more commonly used dispersants are listed in a later section. The mechanism of the action of dispersants in maintaining oil-insolubles in a state of relatively stable suspension may be considered to be analogous to that of emulsifying agents in oil-water systems. Water droplets suspended in an undoped oil coalesce readily, for in so doing they lower the area of the interface and hence the free interfacial energy of the system. When emulsifying agents are present they are adsorbed at the interface of the droplets. The driving force behind this adsorption process is the decrease in free interfacial energy, which in ergs per square centimeter is numerically equal to the decrease in interfacial tension in dynes per centimeter. Because of the fact that the system is at a lower free energy level, and possibly because the adsorbed film offers mechanical protection as well, there is less tendency for droplets to coalesce; hence the emulsion is more stable. In the case of oil-insolubles in oil a similar theory can be used except that the discontinuous phase is a solid instead of a liquid. Figure 14 shows photomicrographs of dispersed and of flocculated sludge particles. It has been suggested that dispersants act through adsorption on the metal surfaces of the engine as well as on the particles of oil-insolubles.[5] However, if this were the case one would expect that metal catalysis and bearing corrosion would be decreased through a pas-



White Oil – Flocculated Sludge



White Oil + Dispersant – Dispersed Sludge

Figure 14. Dark Field Photomicrographs (approximately 500×) of Used Oil after Lauson Engine Test. (Cracked gasoline used as fuel)

sivating action; actually the opposite is true.[29] It must, therefore, be concluded that if dispersants do form an adsorbed film on metal surfaces, the film is not at all impervious to corrosive oxidation products of the oil.

As an alternative to this physical mechanism Denison and Clayton[8] have suggested a chemical theory to account for the action of certain dispersants. According to their theory, lacquer forms on hot surfaces by the condensation of oxyacids which are formed through oxidation of the oil. Basic additives, which are salts of strong bases and weak acids, combine with these stronger oxyacids to form salts. The weak acids liberated in the reaction are not capable of condensation to lacquer.

TABLE 22. EFFECT OF DISPERSANTS IN REDUCING LACQUERING IN 40 HR. LAUSON TEST
(Oil 285°F)

Lubricant	Fuel	Dispersants* In Oil, %	Lacquer Rating
White Oil	Cracked gasoline	0	3.7, 3.4
White Oil	Cracked gasoline	2	10 0, 9 8
Duo-Sol Extracted	Straight run gasoline	0	5 2
Duo-Sol Extracted	Straight run gasoline	2	10.0

* Soap-type additive.

An effective dispersant is capable of preventing the deposition of lacquer originating either in the oil or in the fuel, at least under certain operating conditions. This is illustrated in Table 22. The differences shown in Table 22 are much greater than those shown in Figure 13, demonstrating that 2 per cent of a dispersant of this type is much more effective than a change of 10 or 20 per cent in aromatic or naphthene content in the base stock.

While a given oil has certain solvent and antiflocculant properties when fresh, these properties may undergo profound changes during use in an engine. Both the base stock and the additive may change in this regard. The former will in general become more polar due to the presence of soluble oxidation products, and will, therefore, have a greater tolerance for dissolved or colloidally dispersed sludge. In cases of extreme oxidation this effect may be so pronounced that the addition of fresh oil to the oxidized sample results in copious precipitation. This is particularly true when a fresh paraffinic oil, e.g., Pennsylvania or solvent-extracted Mid-Continent, is added to an

oxidized naphthenic oil, e.g , California, but may also occur when a fresh oil is added to oxidized material of identical original composition. Mougey[19] attributed the formation of "coffee ground" sludge to this mechanism.

There is, in addition to the solvent and dispersant effect imparted by soluble oxidation products, a dispersant effect of soluble metal soaps formed by the action of some of the oxidation products upon engine metals and lead resulting from the combustion of fuels containing tetraethyllead. All these changes are in the direction of decreased tendency toward deposition of oil-insolubles. The possible changes which dispersants undergo during engine operation include thermal decomposition, oxidation, and hydrolysis, and these changes normally result in a loss in antiflocculation properties.

Metal-containing dispersants probably undergo changes during service which are not readily apparent. It is quite conceivable that a metal soap, for example, would undergo oxidation or thermal decomposition, but would then form another soap through combination with an acidic oxidation product of the oil. Such a change could result in an increase or decrease in the effectiveness of the additive. The change would be difficult to detect if the new soap were equally effective as a dispersant. If such reactions are taking place, the important part of most dispersants, as far as the final effect is concerned, is the metal constituent. The organic portion of the molecule may serve only to keep the metal in solution until further reaction takes place. However, it should be understood that an analysis for total ash or for the specific metal contained in an additive does not necessarily indicate the presence of the original additive in a used oil.

Conditions. While the principal effect of engine conditions upon lacquer and sludging is through the formation of insoluble material, there is an additional effect upon the deposition of these products. One condition that appears to be important is the presence of water. In cold operation the presence of water in the crankcase leads to the formation of the so-called "mayonnaise" type of sludge deposit, while lacquer deposits are more likely to form at higher temperatures, in which case there is no water present.

Temperature has a direct effect upon the ability of an oil to dissolve or peptize oxidation products, as well This is illustrated in Figure 15, which is based upon the results of experiments similar

to those described in connection with Figure 13. It will be observed that increasing temperature causes a reduction in asphaltenes retained on the filter, indicating an increase in solvency and/or antiflocculant efficiency. The breaks in the curves for the two doped oils at high temperatures are attributed to decomposition of the dispersant, either through oxidation or thermal effects. For practical

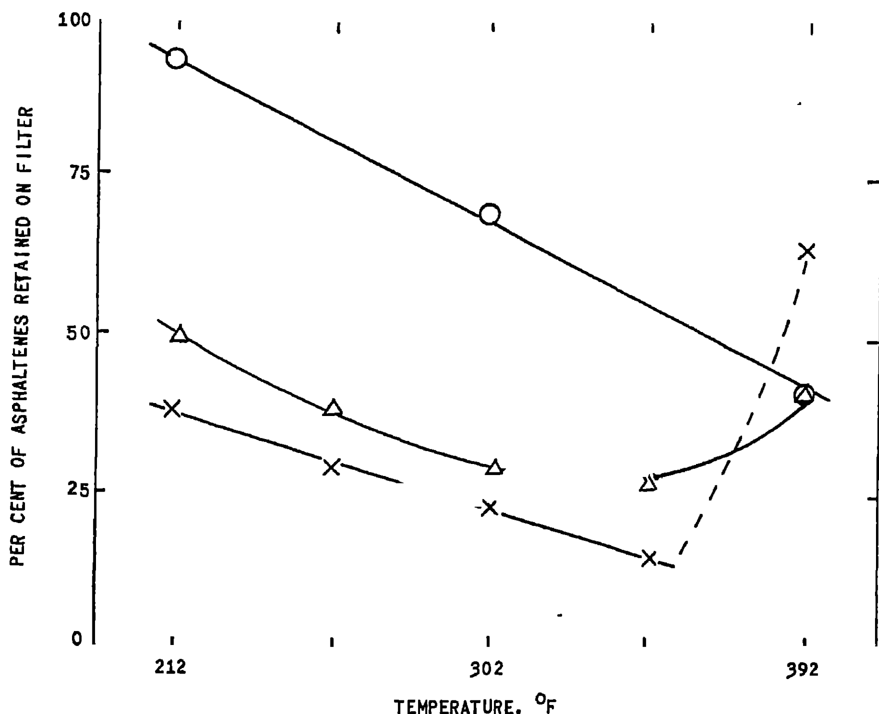


Figure 15. Effect of Temperature on Peptization and/or Solution of Asphaltenes in White Oil (0.1% asphaltenes, 16 hours)

O White Oil
× White Oil + Dispersant A
△ White Oil + Dispersant B

purposes the increase in tolerance for dissolved or dispersed asphaltenes associated with higher temperatures would, of course, be much more than offset by the increased rate of formation of asphaltenes.

Effect of Oil Filters upon Dispersants

Oil filters can be classified into two general types: those which function mechanically, and those which act through adsorption.

For straight mineral oils the latter type offers certain advantages, since within the limits of its capacity it removes harmful soluble oxidation products, e.g., corrosive acids, as well as insoluble sludge particles and extraneous solids. For additive type oils, however, only a mechanical filter should be used, for the adsorption type removes many additives as well as soluble oxidation products by adsorption. Most antioxidants and dispersants would fall in this category. McDonald[16] has shown that a fresh adsorption filter, containing fuller's earth as adsorbent, removed more than 50 per cent of the soap-type additive from a diesel oil in 8 hours of operation, and 80 per cent in 24 hours.

Nutt[22] has shown that all filters remove some additive from an additive oil. He evaluates filters by circulating a clean, fresh oil through them for 100 hours at 160°F and a pressure drop of 20 psi. A removal of 30 per cent of the additive is allowed. He has also shown that finely divided silica, fuller's earth, carborundum, and aluminum can be filtered from a dispersant type oil with approximately the same ease as from a straight mineral oil. Organic deposits originating from the fuel and oil, on the other hand, are held in such a fine state of subdivision by the dispersant, if it is functioning properly, that they pass through mechanical filters. Watkins[26] has pointed out the fact that any molecules of dispersant which are attached to relatively large sludge particles suspended in the oil will be removed upon passage of the oil through a mechanical filter, but that such molecules have accomplished their purpose by keeping the sludge particles suspended until they reach the filter

Evaluation of Additives

Engine Tests. To determine whether or not a given additive will reduce the tendency of a given oil to lacquer, it is necessary only to run engine tests with and without the additive. However, it is possible with the further expenditure of only a relatively small amount of time and effort to evaluate the additive fairly completely with respect to mechanism. Lauson tests, both with the combination of a lacquering oil and a nonlacquering fuel and with the combination of a white oil and a lacquering gasoline, along with laboratory oxygen absorption tests, both with and without metals present, provide sufficient data to supply a reasonably complete picture The behavior of three types of additives in these tests is

summarized in Table 23. The three types behave quite differently when performance under all conditions is considered. It must be recognized, of course, that many commercial additives are mixtures containing two or more of these types; in some instances two or three functions may be included in a single molecule.

The detergent properties of an oil, i.e , the ability to remove previously formed deposits, can be determined by running the oil in a prelacquered engine. McNab *et al.*[17] have reported considerable removal of engine deposits from an automotive diesel engine by the use of an additive which they describe as a detergent-disperser-inhibitor. Georgi[11] has shown that heavy-duty oils, which contain dispersants, exert considerable detergent properties on engine deposits of a soft and grease-like nature which occur where the oil circulation is vigorous. However, he found it necessary to use a material having true solvent action to remove the hard, adherent deposits or the soft deposits occurring in areas where oil flow is limited.

TABLE 23 BEHAVIOR OF DIFFERENT TYPES OF OIL ADDITIVES IN LAUSON ENGINE AND IN LABORATORY OXYGEN ABSORPTION TESTS

Type of Additive in Lubricating Oil	Effect in Lauson Engine				Effect on Rate of Oxygen Absorption in Laboratory Tests	
	Straight Run Fuel, Lacquering Oil		Cracked Fuel, Nonlacquering Oil			
	Quantity of Lacquer	Change in Oil Properties	Quantity of Lacquer	Change in Oil Properties	Metals Present	Metals Absent
Antioxidant	Decrease	Decrease	No change	No change	Decrease	Decrease
Anticatalyst	Decrease	Decrease	No change	No change	Decrease	No change
Dispersant	Decrease	Increase*	Decrease	Increase*	Increase*	No change

* Due to increased metal catalysis.

The relationship between lacquer rating and used oil properties depends almost entirely upon the oil and fuel used With similar oils of varying stability but without added dispersant in conjunction with a nonlacquering fuel, the used oil properties, such as saponification number, neutralization number, change in viscosity, etc. would be expected to parallel the lacquer ratings. The presence of a dispersant would of course upset such correlations, for the lacquering tendency would be reduced while over-all oxidation would in most cases be increased.

When an undoped white oil is run in the Lauson engine with various fuels there is an inverse relationship between lacquering

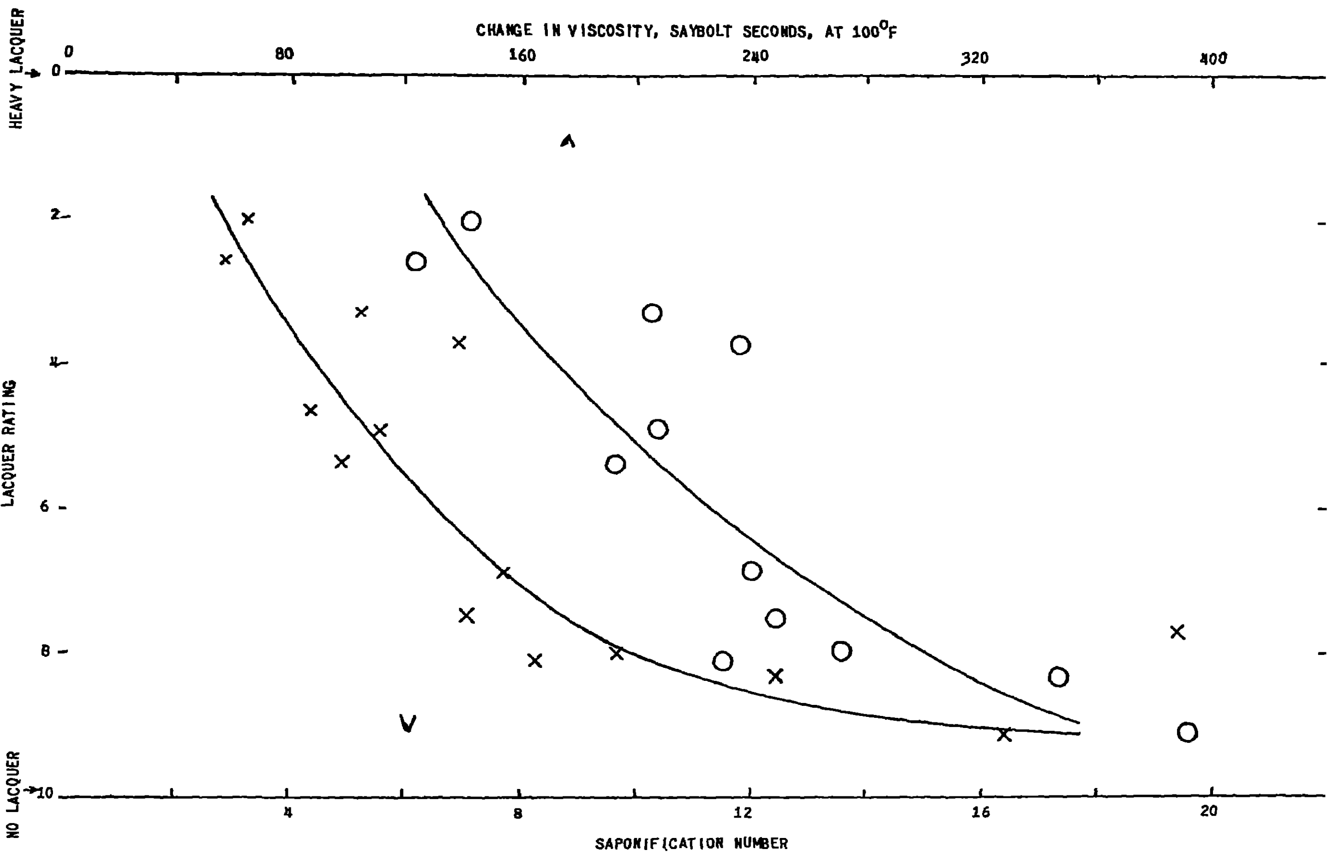


Figure 16. Relationship between Lacquer Rating and Used Oil Properties in Lauson Engine Tests on Undoped White Oil Used in Conjunction with Various Fuels.

and certain used oil properties which are influenced by soluble oxidation products. This is illustrated in Figure 16, in which change in viscosity and saponification number are plotted against lacquer rating for a series of such tests. While there is a considerable scatter-

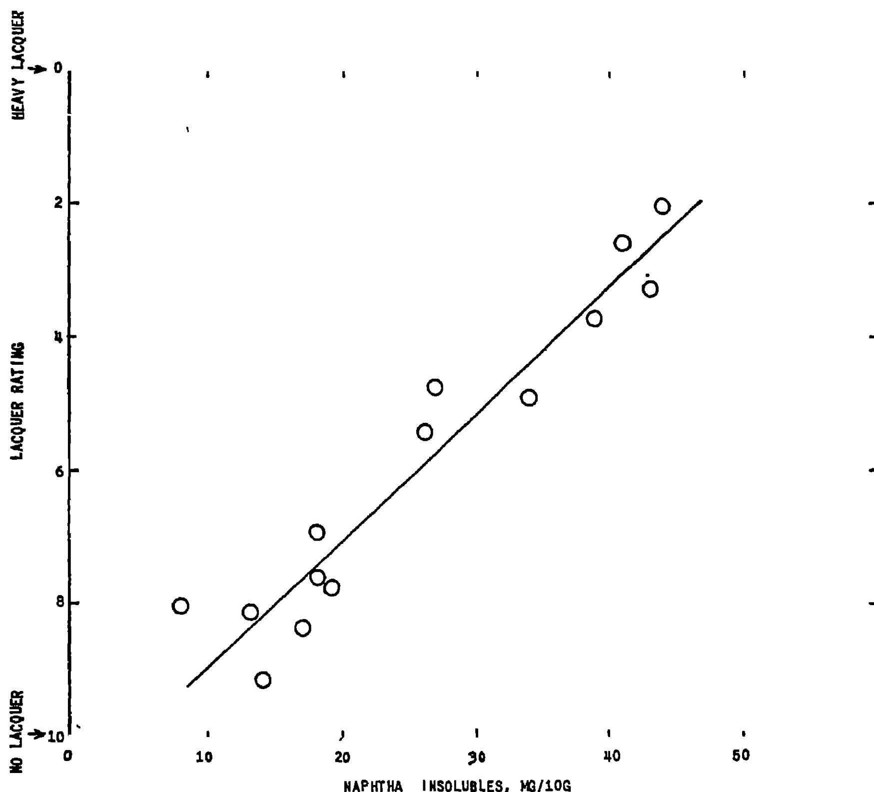


Figure 17. Correlation between Naphtha Insolubles in Used Oil and Lacquer Rating in Lauson Engine.

Lubricant—White Oil
Fuel—Various Gasolines

ing of points, a definite trend is indicated. The increased oxidation accompanying decreased lacquer deposition is attributable to increased metal catalysis by exposed engine parts. There is in this case no direct connection between extent of oxidation of the oil and the quantity of lacquer or oil-insolubles formed, for these originate in the fuel. Correlations similar to those shown in Figure 16 would

be expected if a given oil and fuel were run with varying concentrations or kinds of dispersant.

A general relationship might be expected between lacquer rating and oil-insolubles as determined by high speed centrifugation. Very few, if any, data are available on this point, however, and the nearest approach is the determination of naphtha-insolubles The relationship between oil-insolubles and naphtha-insolubles is not constant. It varies with such factors as composition of the oil, composition of the insolubles, and the presence of dispersants. However, for a given oil and for insolubles from a common source, the factor relating oil-insolubles and naphtha-insolubles should be fairly constant. The relationship between lacquer rating and naphtha-insolubles for white oil run with various fuels is shown in Figure 17.

Laboratory Tests. In laboratory investigations, as in engine testing, it is desirable to distinguish between the formation and the deposition of oil-insolubles. The insolubles may be introduced into the oil by oxidation of the oil itself or they may be added in a preformed state, either in solution in a solvent which is miscible with oil, e.g., asphaltenes dissolved in benzene, or in a solid state, e.g , lampblack. All these methods have their advantages and disadvantages. Oxidation of the oil closely simulates engine behavior as far as the formation of insolubles derived from the oil is concerned. However, it does not take into consideration the effect of fuels. Furthermore, it complicates the evaluation of additives, for antioxidants as well as dispersants reduce the quantity of lacquer or sludge recovered. The use of a benzene solution of asphaltenes, preferably obtained from used engine oils, has the advantage of separating the effects of oxidation and flocculation. This method, namely, of replacing one solvent, in this case benzene, with another in this case lubricating oil, is a standard method for preparing colloidal solutions Its main disadvantage as applied to this problem is the difficulty of obtaining a standard and reproducible source of asphaltenes or oil-insolubles. Lampblack has been used by Talley and Larsen[24] to simulate soot deposits formed in diesel engines. It is probably more easily defined and reproduced than asphaltenes since it more nearly approaches being a definite chemical substance. However, it must be added as a solid and in a state of aggregation outside of the colloidal range.

There are several methods for determining the extent of flocculation of oil-insolubles. The most direct for qualitative purposes is a simple microscopic examination. For quantitative work filtration or high speed centrifugation may be employed. Additional methods are the chromatographic technique used by Talley and Larsen in connection with their studies with lampblack, and effect upon infrared radiation. Talley and Larsen have described four tests which employ various combinations of introduction of oil-insolubles and determination of the degree of peptization The first two employ oxidation of the oil for forming the insolubles and high speed centrifugation and transmission of infrared light of 9700 Ångstrom units wave length, respectively, for detecting peptization. The third is the Wood River method in which a benzene solution of asphaltenes is added to the oil, followed by filtration. The last is the chromatographic method in which lampblack is added to the oil which is then filtered through a column of sand and the depth of penetration by lampblack noted.

Commercial Use of Dispersants

On the basis of the preceding discussion it is possible to formulate the following characteristics which a dispersant should possess:

(1) *Ability to prevent flocculation of oil-insolubles.* This is, of course, the primary requirement of this type of additive.

(2) *Absence of harmful effects upon other properties.* The compound should not adversely affect the physical or chemical properties of the oil, e.g., pour point, viscosity-temperature slope, oxidation stability, corrodibility of bearings, etc.

(3) *Solubility in base stock and compatibility with other additives* The dispersant must not separate from solution at low temperatures and must be compatible with other addition agents such as antioxidants, passivators, pour point depressors, antifoam agents, etc., which may be present in the oil.

(4) *Stability to oxidation, hydrolysis, and high temperatures* Many compounds which are effective dispersants at room temperature fail in practice because of poor thermal stability or ease of oxidation or hydrolysis. The extent of stability required varies with the application.

In addition the dispersant must be available at a low enough cost so that its use is practical

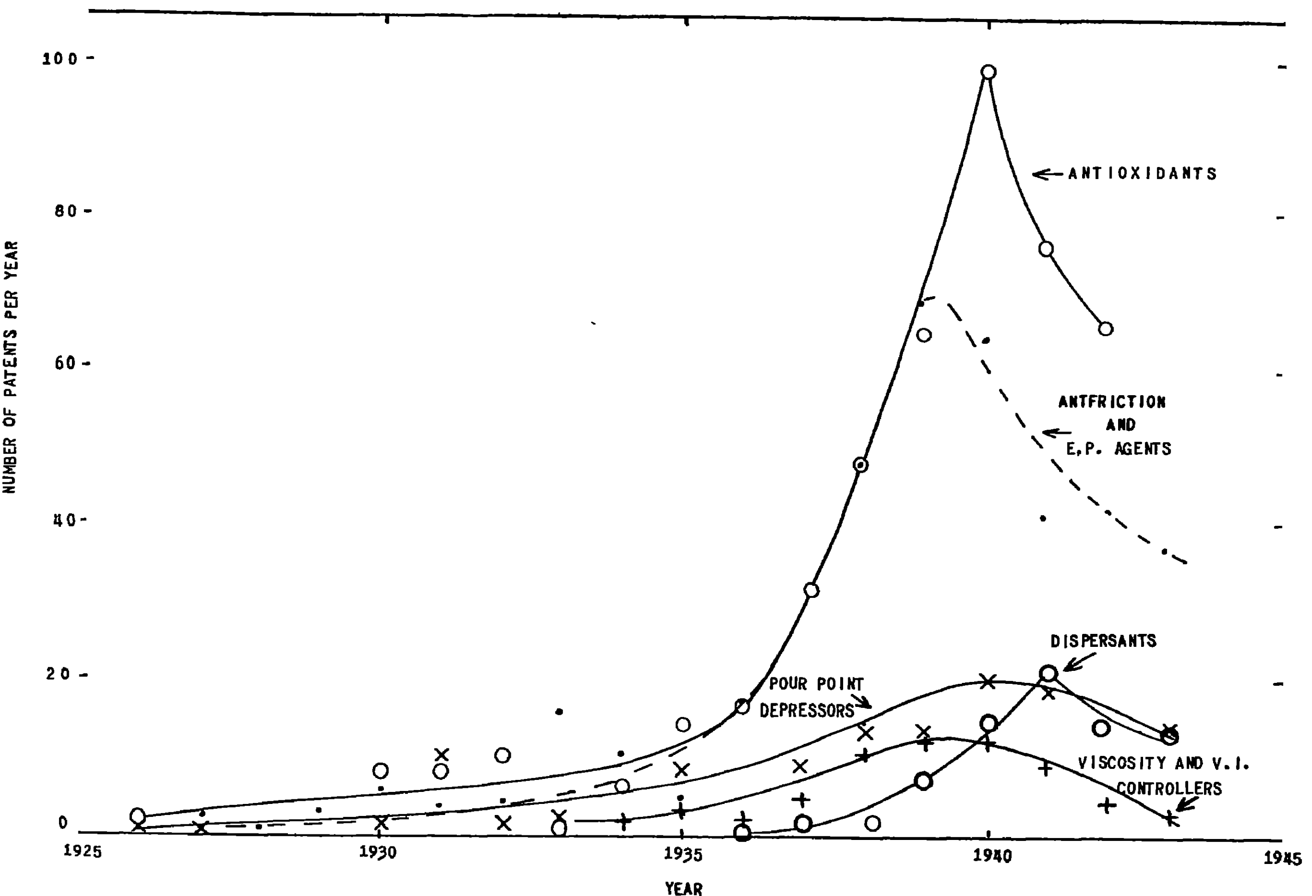


Figure 18 Number of U S. Patents on Lubricating Oil Additives Per Year Versus Date. (Taken from Wright[27])

Of the five types of lubricating oil additives mentioned by Wright,[27] dispersants constitute the most recent development. This is illustrated in Figure 18, taken from Wright's patent survey.

Figure 18 shows that patents on dispersants began later and reached their peak later than the other four classes of additives covered. The decline since 1941 is probably due in part to the war. It will be observed that patents granted on dispersants reached a peak in 1941.

The first commercial oil containing a dispersant was introduced in 1935.[21] However, this oil was recommended for use only in engines equipped with babbitt bearings since it was very corrosive to cadmium-silver and copper-lead. The first dispersant oil which could be used with the newer bearings was introduced in 1939.

Heavy duty engine oils are commonly manufactured by incorporating an antioxidant and a dispersant into a suitable mineral oil base. Georgi[12] lists the following dispersants which are used commercially in such oils: calcium petroleum sulfonate, calcium cetyl phosphate, calcium octyl salicylate, calcium phenyl stearate, the barium salt of wax-substituted benzene sulfonate, the barium salt of wax-substituted phenol carboxylate sulfide, and the potassium salt of the reaction product of phosphorus pentasulfide and polybutene.

Another type of lubricant, known as "Series 2" oil, has recently been developed.[23] This type differs from conventional heavy duty oils in that five to ten times the concentration of additive is used. The use of oils of this type has proven very successful under certain severe conditions, particularly those involving the operation of diesel engines on high-sulfur fuel.[9]

Bibliography

1. Albright, B E., Nelson, F. L , and Raymond, L , *Ind. Eng. Chem* , **41,** 897–906 (1949).
2. Backoff, W. J , *S A.E. Quart. Trans* , **2,** 88–93 (1948).
3 Bouman, C. A , "World Petroleum Congress" Proceedings, Vol. II, pp 248–55, London, 1933.
4 Bowhay, E J , and Koenig, E F , *S.A E Quart Trans* , **2,** 132–47 (1948).
5. Bray, U. B., Moore, C C , and Merrill, D R , *S A E. Journal,* **44,** 35–42 (1939).
6. Cloud, G H , and Blackwood, A J , *S A.E Journal,* **51,** 408–14, 419–20 (1943)
7. C.R C. Handbook, Coordinating Research Council, New York, 1946.
8 Denison, G. H , and Clayton, J O , *S A E Journal,* **53,** 264–8 (1945)
9 Edgar, J A , Plantfeber, J M , and Bergstrom, R. F., *S A E Quart Trans* **3,** 381–9 (1949)

10 Georgi, C. W , *S A.E Journal*, **51**, 52–62 (1943).
11. Georgi, C W., *Petroleum Refiner*, **23**, 504–8 (1944).
12. Georgi, C. W , "Motor Oils and Engine Lubrication," New York, Reinhold Publishing Corp , 1950
13. Gruse, W. A , and Livingstone, C J , "A S T.M. Symposium on Lubricants," pp. 1–28, 1937.
14. Gruse, W A., and Livingston, C. J., *S A E Journal*, **45**, 324, 334 (1939)
15. Kishline, F. F., *S.A.E. Journal*, **45**, 321–4 (1939).
16 McDonald, A. T , *S A.E Journal*, **44**, 23–8 (1939)
17. McNab, J G., Winning, W. C , Baldwin, B. G., and Miller, F. L., *S.A.E Journal*, **49**, 309–25 (1941)
18. Moir, H. L., and Hemmingway, H. L , *S A E. Quart. Trans* , **1**, 389–407 (1947).
19. Mougey, H. C., *S A E Journal*, **53**, 129–37 (1945).
20. Mougey, H C., *S A E. Journal*, **53**, 582–7 (1945).
21. Neely, G L., *S.A E. Journal*, **49**, 464 (1941)
22 Nutt, H V., *S.A E. Journal*, **52**, 573–85 (1944)
23. Symposium on High Additive Content Oils, Special Technical Publication No. 102, A.S T.M., 1950
24. Talley, S K., and Larsen, R G , *Ind. Eng. Chem* , *Anal. Ed.*, **15**, 91–5, (1943).
25 von Fuchs, G H , Wilson, N. B , and Edlund, K. R., *Ind Eng. Chem.*, *Anal Ed.*, **13**, 306–12 (1941)
26. Watkins, F M., *Petroleum Refiner*, **25**, 1–5 (1946).
27. Wright, W A., *Nat. Petroleum News, Technical Sect.*, **37**, R34-8 (1945).
28. Zuidema, H. H., *Chem Rev* , **36**, 197–226 (1946).
29. Zuidema, H H , *Oil Gas J* , **44**, 100–8, Feb. 16, 151–8, Feb 23, 66–72, Mar. 2 (1946).

Chapter VI

EMULSIFICATION AND FOAMING

Introduction

The tendency for an oil to foam or emulsify varies widely with its properties, notably its surface active characteristics. Foaming is in general undesirable in a lubricant. A bearing may fail from lack of lubrication if the oil being pumped through it is momentarily replaced by a pocket of air. Emulsification, on the other hand, may be either desirable or undesirable, depending upon the application. Oils used to lubricate various machines may become contaminated with water. Steam turbine oils are, for example, often contaminated with steam which enters the oil through small leaks and condenses in the oil. Ease of separation of water from the oil is essential, since bearings which are designed for lubrication with oil of a certain viscosity are not satisfactorily lubricated by water or a mixture of oil and appreciable quantities of water. The presence of emulsifying agents in the oil can therefore not be tolerated in this type of installation unless contamination by water and steam can be completely eliminated Oils used in other applications, e.g., "soluble" cutting oils, require the presence of relatively high concentrations of effective emulsifying agents, since they are used in the form of an emulsion. Soluble oil is marketed in the form of an oil concentrate which is emulsified with water prior to use. The ratio of oil to water in the emulsion is normally of the order of 1:20 to 1:50 or 1:60. Lubricants of the emulsion type, since they contain such a large concentration of water, have a much higher specific heat and latent heat of vaporization than anhydrous oils. They are used to good advantage whenever cooling rather than lubricity is of paramount importance.

Theory of Emulsions

An emulsion may be defined as an intimate dispersion of one liquid within another. Such a system is thermodynamically unstable However, the time required for phase separation may vary from seconds to years. The free interfacial energy, which in ergs

per square centimeter of interface is numerically equal to the interfacial tension in dynes per centimeter, acts as a driving force to decrease the interfacial area, i e., by causing small drops to coalesce into larger ones whenever they come in contact with one another as a result of Brownian movement or mechanical agitation. The rate of separation of an emulsion is a function of the initial particle size, the difference in density of the two phases, the viscosity of the continuous phase, and the gravitational constant. The mathematical relationship, known as Stokes' law, is as follows:

$$U = \frac{2}{9} \frac{r^2(d_2 - d_1)g}{\eta}$$

where U is the settling velocity, r is the radius of the droplets, d_2 and d_1 are the respective densities of the two phases, g is the gravitational constant, and η is the viscosity of the continuous phase. Separation of an emulsion of a given initial particle size can be accelerated by increasing the gravitational force through the use of a centrifuge. In many cases it is possible to increase $(d_2 - d_1)$ or to decrease η by the addition of a solute or solvent to the continuous phase. For example, in emulsions of hydrocarbons in water, the density of the aqueous phase, and hence $(d_2 - d_1)$, can be increased by the addition of water-soluble inorganic salts. Furthermore, in emulsions of water in viscous oil it is possible to effect a marked reduction in η by the addition of a hydrocarbon of low viscosity such as pentane or hexane.

If a pure hydrocarbon of low molecular weight, for example hexane, is agitated with pure water, the resulting emulsion is very unstable, since the interfacial tension is high and since $(d_2 - d_1)$ is high and η is low. Lubricating oils are much more viscous than hexane and their density approaches that of water more closely. However, they, too, form unstable emulsions with water provided they are free from polar components. Many compounds such as organic acids and soaps act as emulsifying agents They are effective even when present in minute concentration, since they are adsorbed at the water-oil interface. A very low bulk concentration can result in a very high local concentration at the interface Polar components capable of acting as emulsifiers may find their way into a lubricating oil from the following sources:

(1) *Crude petroleum.* Crude petroleum contains appreciable quantities of naphthenic acids and other polar components. Some of these occur in the lubricating oil fractions and they are not always completely removed by refining. They can act as emulsifiers in their original form. Furthermore, acidic compounds are in many cases precursors for more effective emulsifying agents through the formation of soaps by reaction with metals or metal ions.

(2) *Reaction products formed during refining.* Refining, particularly by sulfuric acid or other chemical means, introduces polar reaction products into the oil These products may not be completely removed in the subsequent steps of the refining process.

(3) *Oxidation of the oil during use* A well refined mineral oil is, when fresh, virtually free from polar impurities. However, deterioration through oxidation during prolonged use may result in the accumulation of appreciable quantities of oil-soluble, polar oxidation products capable of acting as emulsifiers. The rate of formation of these products depends upon the composition of the oil and upon the operating conditions.

(4) *Additives contained in the oil.* Soluble oils owe their ability to emulsify spontaneously with water to the presence of emulsifying agents added specifically for that purpose. Many oils which are not intended to be used as emulsions contain other additives which serve various specific purposes Several types of additives are discussed briefly in Chapter VIII. Some of these contain polar groups and they may act as emulsifiers in addition to performing the function for which they were added.

(5) *Contamination* Oils are subject to contamination by emulsifying agents from extraneous sources during use. For example, certain parts of many machines are lubricated by oil and others by grease. Contamination of the one lubricant by the other is sometimes difficult to avoid. Most lubricating greases contain relatively large concentrations of metal soaps, which, as a class, are notorious as emulsifiers.

Thus if an oil is to possess good initial demulsifying properties, it must be refined in such a manner that polar impurities either initially present or formed in the early steps of the refining process are virtually eliminated. Additives used must be chosen which have the minimum effect upon emulsion properties In order for the oil

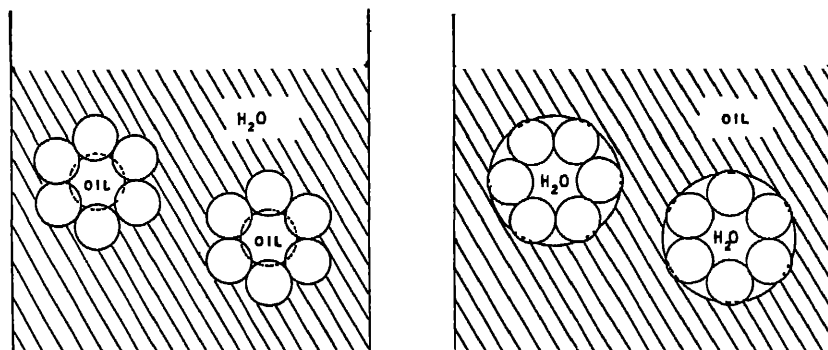
to retain its ability to resist emulsification it is necessary that it be stable toward oxidation under the conditions imposed upon it and that it be protected against extraneous contamination.

Many theories, some which overlap to a certain extent and others which have been discarded, have been proposed to explain the action of emulsifying agents[4, 6] Clayton,[6] for example, discusses six theories: the viscosity, the hydration, the surface tension, the adsorbed film, the oriented wedge, and Roberts' theory. Of the factors considered in these various theories, adsorption of emulsifying agent at the water-oil interface is without a doubt the most fundamental. It is impossible to produce an emulsion of any degree of stability unless an adsorbed film of some kind is present at the interface. Substances which adsorb at the oil-water interface are characterized by an affinity for both phases. They may be simple molecules like organic acids which contain a hydrocarbon group with an affinity for oil and a polar group with an affinity for water. Such molecules tend to orient at the interface with the polar group toward the water phase and the hydrocarbon group toward the oil. Most of the common emulsifiers, e.g., soaps, are complex rather than simple substances, and they exist in a colloidal state rather than in true solution. However, the same requirements regarding mutual affinity for both phases apply. Finely divided solids may also act as emulsifying agents. Here again it is necessary for the solid to have an affinity for both phases, i.e., it must be selectively, but not completely, wetted by one of the liquid phases.

The type of emulsion, oil-in-water or water-in-oil, is determined partially by the volume ratio of the two phases and the manner in which the emulsion is prepared, but largely by the emulsifying agent. In a stable emulsion, the phase which has the greater solubility or wetting power for the emulsifier will in general be the continuous phase. The reason for this is schematically illustrated in Figure 19, which represents two emulsions, both containing a colloidal emulsifier which is preferentially wetted by water, namely an alkali metal soap. *A* is a stable emulsion of oil in water, for the adsorbed soap micelles prevent the oil droplets from touching one another and coalescing *B* is an unstable emulsion of water in oil, since the adsorbed micelles are largely within the water droplets and are therefore ineffective for preventing contact of the droplets.

From this illustration it is clear that there can be no general

correlation between interfacial tension and the stability of emulsions. A high interfacial tension between oil and water denotes little adsorption at the interface and hence an unstable emulsion. A low interfacial tension denotes strong adsorption, but the emulsion may or may not be stable. Stable emulsions of a given type may actually be broken by adding an emulsifier which favors the opposite type. Oil field emulsions of the water-in-oil type are, for example, broken



(A) Stable Emulsion (B) Unstable Emulsion

Figure 19. Effect of Emulsifier upon Type of Stable Emulsion The small circles represent an emulsifier which is preferentially wetted by water.

by the addition of an "antagonistic" emulsifier which favors the oil-in-water type and thus offsets the effect of the naturally occurring emulsifiers which favor the opposite type.

Steam Turbine Oils

The lubricant used in steam turbines constitutes a good example of an oil which is frequently contaminated with water. Turbines are designed to minimize leakage of steam and water into the lubricant, but the occasional presence of water in the oil is not at all uncommon[18]. Turbine oils are, therefore, expected to separate from water rather than forming stable emulsions Gravity settlers, filters, or centrifuges are often used for removing the water from the lubrication system of a turbine[17].

Turbine oils are made by incorporating oxidation inhibitors and rust inhibitors into base stocks of suitable physical characteristics, (viscosity, flash point, etc.) and inhibitor susceptibility. In the selection of each of these three components consideration must be

given to emulsion properties. Rust inhibitors, which are normally polar compounds, are particularly prone to impair the demulsifying properties of the oil.

Laboratory emulsion tests, e g., ASTM Designation D-157-36, Steam Emulsion of Lubricating Oils, are commonly used to evaluate the emulsification properties of turbine oils. While these tests are useful for controlling production at refineries, there is considerable doubt that a correlation exists between the results of any of the existing tests and actual turbine practice.

Soluble Oils

A large volume of oil is used in machine shops in various operations performed on metals, for example, cutting, drilling, grinding, etc. The main requirements of lubricants used for this purpose are fluidity, high specific heat, and good lubricating properties. The relative importance of the last two of these factors depends upon the metallurgy of the material being processed and upon the operation.[14] The heat which is generated when a metal is cut is derived from the following two sources: (1) frictional heat generated between the point of the tool and the surface of the piece being cut and between the face of the tool and the chip which is being removed; (2) heat of deformation of the metal generated by the bending of the chip. The cutting fluid acts as a lubricant to reduce friction and as a coolant to carry away the heat of friction and deformation. It cannot reduce the amount of heat of deformation generated. In operations where the frictional heat is great compared with the heat of deformation, e.g., tapping or broaching, nonaqueous oils are preferred because of their superior lubricating properties. Such oils often contain added antifriction agents, such as fatty oils, and antiwelding agents, such as active sulfur compounds. Where cooling is the principal function, dilute emulsions of oil in water are superior to oil, since water has the higher specific heat and heat of vaporization. Grinding represents an extreme example of an operation in which cooling is of major, and lubrication of minor, importance

The principal requirement of a good soluble cutting oil is that it must emulsify readily with water of varying degrees of hardness to form a relatively stable emulsion. The emulsion must not become rancid or corrosive during use, it must have sufficient lubricity to

satisfy the needs, and it should provide protection against rust. It must also be harmless to the operator.

Soluble oils contain, as their major components, mineral oil and emulsifying agent.[11] The latter are generally sodium soaps of carboxylic acids and/or sodium salts of sulfonic acids. They must be present in high concentration in the oil in order to provide sufficient concentration in the final dilute emulsion of oil in water. Other additives, e g., rust preventives, antioxidants, and germicides, may be added. Water and mutual solvents for oil and water may also be present.

Most soluble oils form white, opaque emulsions which resemble milk in appearance. However, it is possible to make transparent emulsions by choosing the components so that both phases have essentially the same refractive index. A reasonable degree of transparency can be attained with phases of different refractive index by reducing the interfacial tension to a very low level with sufficient emulsifier of the proper type, thus affecting a degree of dispersion approaching the colloidal state. Transparent cutting oils or cutting oil emulsions have the practical advantage that they do not mask the work from the vision of the operator.

Theory of Foams. There are many points of similarity between emulsions and foams. Both consist of one phase dispersed within another and both require the presence of an adsorbed film at the junction between the two phases for stability. Both may be stabilized by the addition of certain polar compounds and broken by the addition of others. Foams differ from emulsions in that the dispersed phase is a gas rather than a liquid and thus has no solvent properties for any polar substances present in the liquid-gas boundary. Furthermore the gas bubbles in a foam, unlike the liquid droplets in an emulsion, are subject to appreciable changes in volume with relatively small changes in temperature or pressure which may be imposed upon the system. These differences make it necessary to work out theories of foam somewhat different from those used for emulsions.

While viscosity is an important factor in foam stability,[5] pure liquids, regardless of how viscous they are, do not produce stable foams, for it is impossible for them to form films differing in composition from the bulk of the liquid phase.[1] However, the formation of foams does not require the presence of polar components in the

system. Binary solutions containing both an aromatic and an aliphatic hydrocarbon are capable of foaming, although neither component foams when tested alone.[12] Lubricating oils can likewise produce foam of appreciable stability even though they are devoid of polar components, for they are complex mixtures of hydrocarbons.

Much of the experimental and theoretical work on foaming has been in connection with boiler water problems. Foulk,[7] who was working in this field, proposed a "balanced layer" theory to account for foaming. According to this theory, foams owe their stability to a surface film which is either richer or poorer in solute than the bulk liquid; i.e., adsorption of solute, either positive or negative, has taken place. These two conditions are schematically illustrated in Figure 20. Since adsorption in both cases takes place spontaneously, i.e., with a decrease in free energy, free energy must be added to the system in order to "redissolve" the films in the bulk liquid. Thus the greater the difference in concentration of solute in the surface film and in the bulk, the greater the stability of the foam.

Foulk explains the action of certain antifoam agents in terms of this theory to be the result of a balance between positive and negative adsorption. Thus a foam stabilized by positive adsorption can be broken by the addition of the proper concentration of negatively adsorbed substance, and vice versa.

Foulk and Miller[8] published experimental data to support the balanced layer theory. They measured the foaming tendency of aqueous solutions of sulfuric acid and of several inorganic salts. They also determined the surface tension of each solution, both by the vibrating jet and the drop weight methods. The former measures the surface tension of a fresh surface under dynamic conditions, while the latter deals with a somewhat aged surface under substantially static, or equilibrium, conditions. Adsorption, either positive or negative, should result in a difference between the two surface tension values on a given solution. Since adsorption is, according to the theory, also responsible for foaming, it follows that foaming should correlate with the difference in surface tension by the two methods Foulk and Miller actually showed such a correlation. However, most of their static surface tension values are higher than the corresponding dynamic values. The data are therefore not compatible with the generally accepted theory that adsorption takes place because of the decrease in free surface energy which ac-

companies a decrease in surface tension. If this theory is correct, and there is much evidence to support it, the surface tension of a

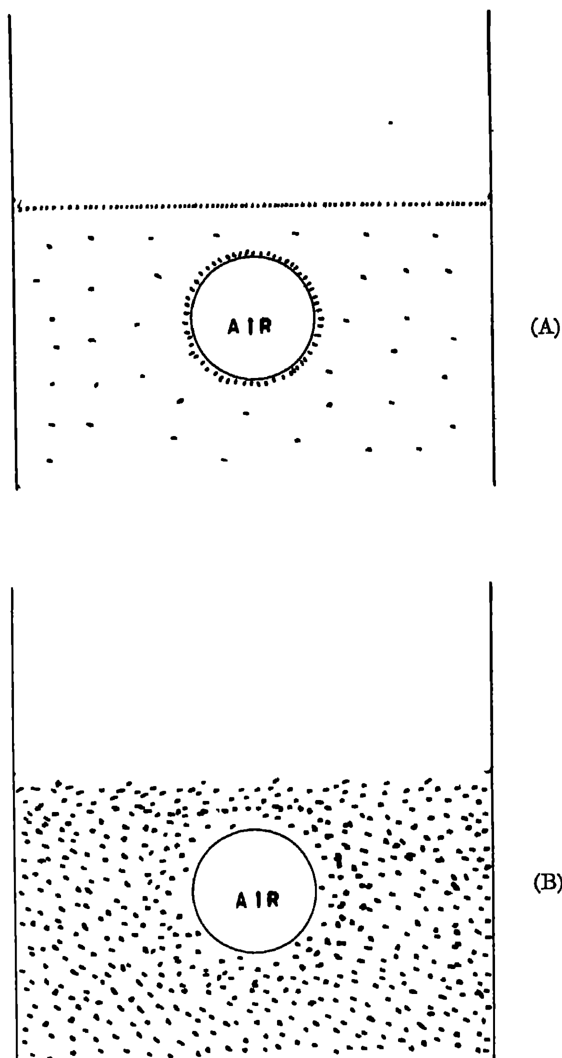


Figure 20. Positive and Negative Adsorption in Surface Films (A) Positive Adsorption; (B) Negative Adsorption.

given liquid must, in the absence of chemical changes, either remain constant with respect to time in the case of zero adsorption or decrease with time in the case of either positive or negative ad-

sorption. This requires that the static surface tension always be equal to or less than the dynamic value. The data of Foulk and Miller, therefore, neither prove nor disprove the balanced layer theory. The theory is, however, quite plausible and is capable of explaining many of the known facts regarding the behavior of foams.

Jacoby, who like Foulk worked on the problem of foaming in boiler water, has proposed an interesting theory of antifoam action.[9] He pictures the double-faced bubble film which constitutes a foam as being subjected to a thinning action caused by the drainage of liquid. When the film reaches a critical minimum thickness it ruptures. Certain polar compounds which are capable of stabilizing the bubble film when present in a liquid state lose this property after some of the liquid has drained from the film This is believed to be due to syneresis, which leaves the adsorbed substance in a solid, brittle, state in contrast to the fluid, elastic, state that prevailed before drainage. According to this theory, one of the necessary conditions for a stable foam is an adsorbed film of great mobility. If this mobility is lost as a result of drainage as described above, the film is easily ruptured.

Trautman[15] has reported some interesting data on the effect of the addition of low concentrations of silicones* upon the foaming characteristics of lubricating oil and other petroleum fractions. The particular silicone used was virtually insoluble in the lubricating oils tested, and concentrations as low as five parts per million or less were quite effective in suppressing foaming. Trautman showed, however, that in the case of a gas oil in which the silicone was soluble to the extent of 0.01 per cent, the addition of silicone below the limit of solubility increased foam stability. Increasing the amount of silicone beyond 0.01 per cent resulted in a decrease in stability of the foam. This indicates that silicones are effective as antifoams only when present in concentrations exceeding their solubility. This observation is consistent with the theory of Jacoby. As long as the adsorbed silicone is in equilibrium with a partially saturated solution of silicone in oil it behaves as a fluid film and stabilizes the foam. Addition of silicone beyond the limit of solubility causes the film to build up to a point where it loses its elasticity, thus causing the foam to collapse.

* Silicones are described in Chapter VIII.

Several compounds claimed to possess antifoam properties when added to lubricating oils are mentioned in the patent literature. These include, in addition to the silicones[10, 16], calcium soaps of wool olein, sodium alkyl esters of sulfuric acid,[2] potassium oleate,[13] and esters of sulfonated ricinoleic acid.[3]

Bibliography

1. Adam, N. K., "The Physics and Chemistry of Surfaces," 3rd Ed , p 142, London, Oxford University Press, 1941
2 Barton, C. H., and Hughes, T. P , British Patent 564,281 (1944).
3. Bennett, H. T., and Marshall, J. R , U S Patents 2,390,491 and 2,390,492 (1945).
4. Berkman, Sophia, and Egloff, Gustav, "Emulsions and Foams," New York, Reinhold Publishing Corp., 1941.
5. Brady, A P , and Ross, Sydney, *J. Am Chem Soc* , **66**, 1348–56 (1944).
6. Clayton, Wm , "The Theory of Emulsions and Their Technical Treatment," Philadelphia, P Blakiston's Son and Co., 1935.
7. Foulk, C. W., *Ind Eng. Chem* , **21**, 815–17 (1929)
8. Foulk, C W , and Miller, J N., *Ind Eng. Chem* , **23**, 1283–8 (1931).
9. Jacoby, A L , *J. Phys. & Colloid Chem.*, **52**, 689–94 (1948).
10. Larsen, R G., and Diamond, H , U. S Patent 2,375,007 (1945)
11 Miller, J. F , *J. Inst Petroleum Tech* , **24**, 645–9 (1938).
12. Robinson, J V , and Woods, W. W., *J. Phys & Colloid Chem* , **52**, 763–6 (1948)
13 Smith, H. G., U. S. Patent 2,377,654 (1945).
14. Swift, H. W., *J. Inst Petroleum Tech* , **24**, 662–7 (1938).
15 Trautman, C. E., *Lubrication Engineering*, **2**, 143–6 (1946).
16. Trautman, C. E., and Ambrose, H. A , U. S Patents 2,416,503–4 (1947).
17 von Fuchs, G H , Wilson, N B., and Edlund, K R., *Ind. Eng. Chem , Anal. Ed* , **13**, 306–12 (1941)
18. Wilson, C. D., *A.S.T M Bull. No 152*, 66–70, May, 1948.

Chapter VII

WEAR

Introduction

In the operation of a machine it is essential that the rate of wear of the moving parts be held to a minimum. Most machines are built to close tolerances, and excessive wear of a bearing or a piston ring necessitates replacement of the worn part. This may require a major overhaul of the machine at a considerable cost in parts, labor, and lost operating time.

Wear, like many other phenomena which take place when a machine is operated, is influenced by the design of the machine, the operating conditions, and the lubricating oil. In order to formulate lubricants which give maximum protection against wear it is essential that the effect of design and operating conditions, as well as the influence of oil factors, be understood.

Types of Wear

Wear can proceed by different mechanisms. The wear of piston rings in an engine operating under low temperature conditions is, for example, an entirely different phenomenon from the wear of gear teeth operating under high pressures. Dayton[16] has classified wear into the following five fundamental types:* (1) cutting by rough surfaces; (2) abrasion by hard particles; (3) galling or scuffing caused by molecular forces; (4) corrosive wear by chemically active substances; (5) fatigue pitting or cracking.

(1) *Cutting.* When a hard rough surface is rubbed against a softer metal, particles of the latter are removed by a cutting action. Wear of this type is negligible unless the two moving parts differ widely in hardness, since the cutting edges are themselves worn down after a relatively short period of operation. From a practical point of view, this type of wear is the least important of the five.

(2) *Abrasion.* Abrasive wear is quite a general phenomenon. It is more complicated than cutting wear in that a third solid component

* The definitions presented here do not necessarily conform to those found elsewhere in the literature. There is considerable variation in nomenclature in this field

is involved. The grit responsible for abrasive wear may consist of particles of metal or their oxides, dust, sand, clay, or any other hard, solid contamination. If the moving surfaces are both relatively hard, e.g., gear teeth, the particles flow along with the oil and cause preferential wear of the softer of the two surfaces. If, on the other hand, the one surface is much softer than the other, e.g., a babbitt journal bearing guiding a steel shaft, the hard particles become partially embedded in the soft bearing and cause preferential wear of the hard shaft. The extent of wear depends upon the ability of the bearing metal to embed the abrasive particles and upon the size and shape of the particles and their hardness with respect to that of the shaft. Particles with sharp edges can roughen and score a steel shaft if they are not sufficiently embedded. If they are almost completely embedded they merely remove the high spots on the shaft and give it a high polish.

(3) *Galling or scuffing.* The welding together of portions of two surfaces, followed by a tearing away of relatively large particles of metal, is known as galling or scuffing. While this type of wear is not as common as abrasion, it is of a much more serious nature when it does occur. Abrasive wear is, as a rule, a slow, cumulative process, while galling may result in almost instantaneous failure. Galling takes place only when conditions allow the two surfaces to approach each other closely enough so that intermolecular forces apply. It is favored by high temperatures and pressures and by clean surfaces. The presence of a film, e g , that formed by an extreme pressure lubricant, permits operation at much more severe conditions of temperature and pressure. Conversely, surfaces which have been subjected to abrasion are particularly susceptible to galling. Dayton[16] found that the pressure required to cause galling in a laboratory test could be greatly reduced by the presence of grit in the lubricant. Some surfaces were much more sensitive to the action of grit than others. Dayton found, for example, that a lapped steel surface could withstand almost three times as much pressure as a ground surface before galling occurred, provided the lubricant was free from grit. The addition of grit up to one per cent in the lubricant had no appreciable effect upon galling in the case of the ground surface, but the presence of as little as one hundreth of a per cent in the case of the lapped surface reduced the allowable pressure by a factor of two to three.

(4) *Corrosive wear.* When an oil contains components which can combine chemically with a metal, wear of a corrosive nature can occur. Moderate corrosive wear, e g., that promoted by extreme pressure agents, may be beneficial in that it prevents galling. Excessive corrosion is, on the other hand, highly objectionable. Corrosive wear, like galling, may be aggravated by abrasive wear which leaves the surfaces vulnerable to attack. The products of corrosion may themselves act as abrasives, e.g., iron oxide or copper sulfide particles.

The corrosion of bearing metals by organic acids dissolved in the oil, by aqeuous acids, and by sulfur compounds, has already been discussed in Chapter IV. Ferrous metals are likewise subject to corrosive wear, particularly by aqueous acids. Williams[29] has shown that cylinder and piston ring wear in internal combustion engines occurs largely during the warm-up period. He concluded that corrosion, induced by condensed water vapor in the combustion chamber, is responsible. The condition is aggravated by water-soluble acids, which may include carbonic acid and low molecular weight carboxylic acids resulting from the combustion of hydrocarbons; sulfurous and sulfuric acids resulting from combustion of sulfur compounds in the fuel, and nitrogen acids formed in small amounts from atmospheric nitrogen in the combustion process. In the case of engines burning leaded gasoline, halogen acids, particularly hydrobromic acid, formed by combustion of the halide scavenger which is present in tetraethyllead fluid, also contribute to corrosive wear

(5) *Fatigue.* Metals fail through fatigue when they are subjected to excessive local stresses. Babbitt bearings will crack and eventually disintegrate when the shaft they support is loaded beyond a certain limit. This type of failure is frequently encountered in heavily loaded or poorly aligned gears. Most investigators do not consider it as a type of wear, but rather as a type of mechanical failure.

Measurement of Wear

Several methods have been devised by various investigators for the quantitative determination of wear, the most common of which measure change in weight or dimensions. The weight measurement method is frequently used in the case of small parts which can be weighed on an analytical balance; the dimension measurement method may be used for larger parts as well. Williams,[29] for example,

determined the wear of cylinder rings gravimetrically and that of cylinders by means of a gage capable of measuring to an accuracy of ±0.002 mm. An instrument known as the McKee gage, developed at the Bureau of Standards, is claimed to be even more sensitive.[10] This gage determines wear by measuring changes in the length of indentations made prior to the test with a precisely shaped tool.

Boerlage and Gravesteyn[8] and Everett and Keller[18] measured cylinder and ring wear by examining the used crankcase oil rather than the engine parts. In this method, based on iron analysis, it is assumed that wear of other ferrous parts of the engine which are lubricated by the crankcase oil is negligible and that virtually all the metal worn from the cylinders and piston rings remains uniformly suspended or dissolved in the oil. These assumptions have been questioned, and the method has not been universally accepted. However, Boerlage and Gravesteyn showed good agreement between total wear calculated from analysis of the oil and that determined by direct measurement of the engine parts. The oil analysis method has the big advantage of permitting the determination of a wear vs. time curve throughout an engine test. Such a curve is easily obtainable from data on small representative oil samples taken at intervals during the test. The method of Everett and Keller consists of ashing a 10 g sample of oil, dissolving the ash in hydrochloric acid, adding ammonium thiocyanate, and determining iron colorimetrically.

Other methods that have been used to detect wear include x-ray diffraction, electron diffraction, and radioactive tracer techniques. Clark, Sterrett, and Lincoln[13] used x-ray diffraction in studying the wear of brass pins used in the Almen machine. These pins had a fiber structure, with the "fiber axis" parallel to the axis of the pin. Forces acting on the pin during the Almen test (see Figure 2, Chapter 1) are perpendicular to this axis and result in a new perpendicular fiber axis. X-ray diffraction detects the change in fiber structure which is in turn an indication of wear. Finch and Zahoorbux[19] employed electron diffraction to study changes in metal surfaces caused by wear. The transformation from a crystalline structure formed by cutting or abrading to an amorphous surface (Beilby layer) by polishing is readily detected by electron diffraction. Pinotti, Hull, and McLauglin[22a] studied piston ring wear by irradiating cast iron piston rings and measuring the radioactivity of the used crankcase oil.

Wear may be measured on parts taken from full-scale engines or smaller test engines or in bench-scale apparatus specifically designed for the purpose. These include bench-scale gear tests and the bench tests described in Chapter I.

Prevention of Wear

The complete elimination of wear constitutes an ideal rather than a practical goal. However, there are several approaches by which rate of wear can be reduced to a satisfactory level. The factors which determine rate of wear can be classified into two main types, (1) mechanical factors, and (2) lubricant and fuel factors.

Mechanical Factors. *Choice of Materials.* Wear can often be reduced by a proper choice of the metals comprising the moving parts. Softer metals are in general more rapidly worn than harder ones. There is, however, no direct relationship between hardness and resistance to wear. According to Poppinga,[28] the most wear-resistant cast iron consists of a uniform pearlite matrix which contains graphite in a fine laminar form. The wear resistance of ferrous metals can also be improved by the incorporation of phosphorus into the alloy or by surface treatment, e.g., nitriding or chromium plating.[28]

The optimum wear-resisting composition for a given application depends to a large extent upon the type of wear which predominates. For example, the best composition for heavily loaded gear teeth might be quite different from that for piston rings and cylinders for an internal combustion engine operating intermittently at low ambient temperatures, in which case corrosive wear predominates.

In actual practice the composition chosen for a given machine part is influenced by many factors other than wear. Such properties as structural strength and weight are important, along with cost and availability. The final selection is often a compromise between minimum wear and optimum performance in other respects.

Surface Finish. Surface finish is a particularly important factor in determinining the initial rate of wear, i.e., during the "break-in" period. If the harder of two hard rubbing surfaces has a rough initial finish, considerable cutting wear of the softer surface may take place before the rough surface is itself worn smooth. In the case of a hard shaft rotating in a soft bearing which is capable of embedding abrasive particles, the initial wear of the shaft itself is governed by its surface finish. Burwell, Kaye, and van Nymegen[11] determined

the rate of wear during the running-in process on steel shafts ground to various surface finishes. The shafts were guided by babbitt bearings. Both the initial rate of wear and the total amount of iron removed were found to be determined by the initial surface roughness. After two hours of running the rate of wear was negligible in all cases. The greatest wear was obtained on a shaft ground to a surface finish of 75 microinches, as measured with a profilometer, and the least with a "superfinished" shaft[27] which had a roughness of only one microinch.

While the smoothest possible surface is highly desirable in certain instances, for example the one cited above, there are other applications in which surfaces with a certain degree of roughness are preferred. Decreased adhesion between metal surface and lubricant film may result from excessive smoothness of the surface.[28] It has been reported that excessive smoothness in cylinder bores results in a rapid destruction of the surface.[28]

Operating Conditions. Conditions of pressure, temperature, and rubbing velocity can have profound effects upon rate of wear. Increased pressure tends to reduce the thickness of the film of lubricant between the moving surfaces and thus increases the extent of metal-to-metal contact and wear. Excessively high temperatures may cause increased mechanical wear due to a decrease in viscosity of the oil. Too low a temperature may, on the other hand, lead to corrosive wear by condensed moisture or dilute aqueous acids. The wear of piston rings and cylinders, which normally constitutes the most serious source of wear in internal combustion engines, occurs largely by this mechanism.[29] The temperature of the cooling water and of the oil sump are therefore of vital importance.* Speed, like temperature, can have a dual effect upon rate of wear. In heavily loaded bearings, speeds approaching zero constitute a very severe condition, since the ZN/P function (Figure 1, Chapter 1) also approaches zero and the coefficient of friction is very high. Excessively high speeds may result in galling through over-heating at local points of contact. From a standpoint of wear, moderate temperatures and pressures are therefore to be preferred In practice it is often necessary to deviate from optimum conditions for wear in order to achieve high efficiency or maximum power from a machine of a given size

* The effect of temperature is further discussed in the section. Lubricant and Fuel Factors, Fuel.

The use of oil filters to remove particles of grit constitutes a simple means of preventing excessive abrasive wear. Williams[29] ran engine tests on used crankcase oils taken from commercial vehicles. He found that the samples of high ash content resulted in higher rates of cylinder and piston ring wear than those of low ash content, although there was no close correlation. Filtration of the used oils reduced the rate of wear to that of the new lubricant.

Internal combustion engines may pick up grit from the intake air. Cattaneo and Starkman[12] cited an example in which operation of a light airplane for only 25 hours from a sandy landing strip resulted in very severe abrasive wear of the piston rings. One side of one of the rings was reduced in thickness to less than one half of its original dimension. Filters on intake air lines remove much of the sand and dust which would otherwise enter the engine and contribute to excessive abrasion.

Lubricant and Fuel Factors. *Viscosity of the Lubricant.* Under conditions of constant pressure and speed, the function ZN/P is determined solely by the viscosity of the oil. As the viscosity decreases, the thickness of the oil film decreases until the boundary condition is eventually reached. As the moving parts approach each other, the probability of metal-to-metal contact and wear increases. Viscosity would, therefore, be expected to have an inverse effect upon rate of wear. Such an effect has been verified experimentally, although the magnitude of the effect is not great under conditions of abrasive wear Williams[28, 29] found, in engine tests run under abrasive wear conditions, that a difference in viscosity of about 100 Redwood seconds at 140°F was required to cause a noticeable difference in wear of the cylinders and piston rings. This difference in viscosity corresponds roughly to a difference between SAE 10 and 30 or between SAE 20 and 40. Everett[17] ran similar tests upon a series of oils of somewhat wider viscosity range, viz , from SAE 70 down to lighter than SAE 10. He found a low magnitude of wear, as would be expected under noncorrosive conditions, and the precision of the tests was rather poor. However, the average results for several engine tests on each lubricant showed a small but definite trend toward decreasing wear with increasing viscosity. The SAE 10, for example, showed an average wear approximately 4 per cent higher than the SAE 20, and the SAE 30, 10 per cent lower than the SAE 20.

Williams[28, 29] found that viscosity has a much greater effect upon rate of wear of cylinders and piston rings under conditions favoring corrosive wear, i.e., frequent starting and stopping or continuous running under cold conditions. Two oils of 10 and 50 SAE grades, which showed only small differences in abrasive wear, showed differences by a factor of two in one test and a factor of six in another. The lighter oil allowed the greater wear in both cases. Williams further demonstrated the effect of viscosity upon rate of corrosion by dipping strips of cast iron in oils of varying viscosity, allowing the oil films to drain, and then exposing the strips to condensing steam for a prescribed length of time. The extent of corrosion was found to be inversely related to the viscosity of the oil. Williams pointed out, however, that in the engine test he employed there was very little delay in flow of oil to the cylinders at the start of the test In actual practice there is normally some delay, and the advantage of a heavy oil in combatting corrosive wear may be partially offset by the greater delay in supplying oil to the cylinder walls.

Polar Lubricating Oil Additives. Since wear is essentially a phenomenon resulting from friction, it might be expected that any polar agent capable of reducing friction under boundary conditions would simultaneously reduce wear However, it has been shown that there is no correlation between friction and wear.[20, 21] Some additives are effective in reducing friction but have little effect upon wear, while others reduce wear but have little effect upon friction. As Beeck has pointed out,[4] the lack of correlation is probably due to the fact that wear takes place momentarily at isolated spots, whereas friction as normally measured is an average for a larger area and a longer time interval.

Larsen and Perry[20] showed in tests in the four-ball apparatus that acids, e.g., oleic acid, reduce friction but may have relatively little effect upon rate of wear. The latter observation is consistent with the observation of Williams[29] that the addition of oleic or palmitic acid to an oil has little effect upon cylinder and piston ring wear in an engine subjected to conditions favoring abrasive wear. Williams showed, however, that the addition of these same acids to a white oil reduced corrosive wear. This would indicate that the effect of polar additives, like that of viscosity, is more important under corrosive than under abrasive wear conditions. Davis, Sibley, and Lincoln,[15] on the other hand, reported a reduction in wear of about

50 per cent by the addition of methyldichlorostearate, both during starting tests, which would be conducive to corrosive wear, and during hot running, in which abrasive rather than corrosive wear would predominate.

The addition of graphite to an oil will likewise reduce the rate of corrosive wear. A marked reduction in piston ring and cylinder wear has been demonstrated for colloidal graphite added in one per cent concentration to an oil.[28]

Chemical Polishing Agents in the Lubricant. As mentioned in Chapter I, Beeck and co-workers[4, 5, 6] have shown that the action of certain antiwear agents can readily be explained by a chemical polishing theory. They found that tricresyl phosphate, which is a well-known antiwear agent, is effective only on steel or other metals capable of reacting with the additive to form a lower melting alloy On gold and tungsten, tricresyl phosphate is ineffective. According to the chemical polishing theory a local "hot spot", caused by friction, results in the reaction of the additive with the metal to form a lower-melting alloy which is deformed by plastic flow to allow a new distribution of the load. Certain compounds of arsenic and antimony behave in a manner similar to that of tricresyl phosphate. Under the conditions used by Beeck, i.e., those of the four-ball apparatus, the better chemical polishing agents reduced the wear allowed by white oil by a factor of the order of 5 to 10. Polar compounds in white oil were found to be relatively ineffective under these conditions. However, combinations of chemical polishing agents and polar compounds were about twice as effective as the former alone and twenty times as effective as the latter alone.

EP Agents. EP agents prevent galling or scuffing under extreme conditions of temperature and pressure. They do not prevent wear in the ordinary sense; in fact they ordinarily promote a certain degree of corrosive wear in order to be effective. A classification of the various types of EP lubricants and theories for the mechanism of their action are presented in Chapter I.

Fuel. The effect of various gasoline factors, including sulfur and tetraethyllead content, upon the wear of cylinders and piston rings has been studied in considerable detail by Williams,[29] who used engines which had a bore and stroke of 85 5 mm and which were fitted with thermocouples for measuring cylinder wall temperature He concluded that accelerated wear is caused by the presence of acid-bearing moisture which condenses on the cylinder walls when

the engine is operated at low temperatures, particularly during the warm-up period. The acids which may be present include both

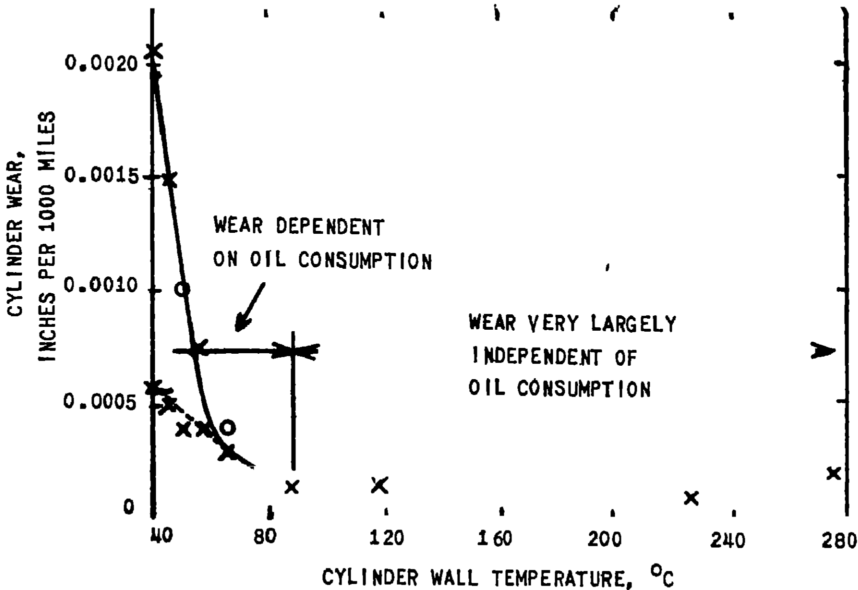


Figure 21 Cylinder Wear in Relation to Cylinder Wall Temperature (Taken from Williams[29])

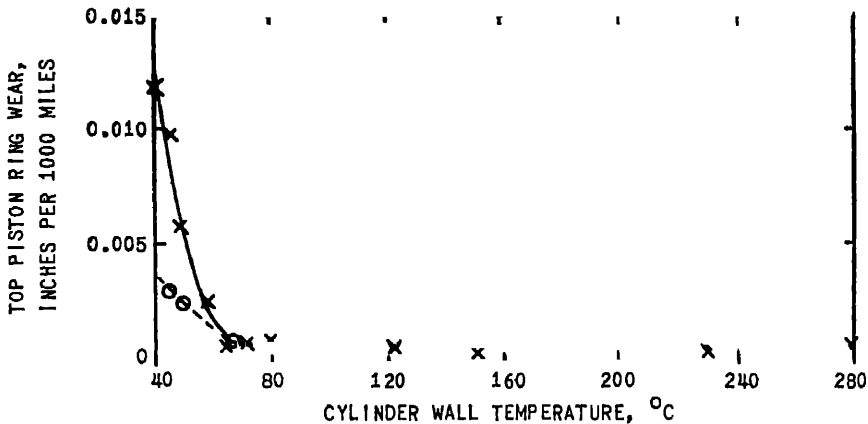


Figure 22 Piston Ring Wear in Relation to Cylinder Wall Temperature (Taken from Williams[29])

organic and inorganic acids, e.g , carbonic and low molecular weight carboxylic acids such as formic and acetic, and acids of nitrogen, halogens, and sulfur. The organic acids are formed by combustion

of the hydrocarbons comprising the bulk of the gasoline. The acids of nitrogen, halogens, and sulfur originate, respectively, from nitrogen in the air, halides in the tetraethyllead fluid, and sulfur compounds in the gasoline. Little, if any, control can be exercised over the formation of organic acids and the acids of nitrogen by altering the composition of the fuel. However, the formation of acids of sulfur and halogens can be influenced by changing the sulfur and halogen content of the fuel.

The effect of fuel factors upon corrosive wear is closely associated with temperature. The effect of cylinder wall temperature upon cylinder and ring wear is shown in Figures 21 and 22, which are based on Williams' data. It will be observed that wear is very low and virtually constant at temperatures above 80 to 90°C., but increases sharply at lower temperatures. This is attributed to corrosive attack by dilute aqueous acids at temperatures low enough to allow their presence in the liquid state at the pressure prevailing in the cylinder.

Sulfur, as shown in Figures 23 and 24 which are also based on Williams' data, has an accelerating effect upon corrosive wear. The data for the 0.1 per cent sulfur fuel were not considered in drawing the curves in these figures since their validity seems to be open to question. Cattaneo and Starkman[12] studied the effect of sulfur over a wider range, viz., 0 to 0.4 per cent, in the FL-2 test, which is run in a Chevrolet engine at a jacket temperature of 95°F (35°C), and found a linear relationship over the entire range. Their results, like the curves in Figures 23 and 24, indicate that wear is approximately doubled by increasing the sulfur content from 0 to 0.1 per cent.

On the basis of preliminary results by Williams shown in Figures 25 and 26, the effect of tetraethyllead appears to be of a smaller order of magnitude than the effect of sulfur. However, Cattaneo and Starkman[12] found a more serious effect. They found that the addition of tetraethyllead fluid in an average automotive concentration, which would be of the order of one to two cc/gal, approximately doubled the rate of wear. They showed, further, that the effect is caused by the halide scavenging agent rather than the tetraethyllead itself. Ethylene bromide in a concentration corresponding to that present in an aviation gasoline containing 4.6 cc/gal of tetraethyllead caused an 8-fold increase in rate of wear. In the presence of the tetraethyllead the effect is less, since most of the bromine combines with the lead rather than forming free hydrobromic acid.

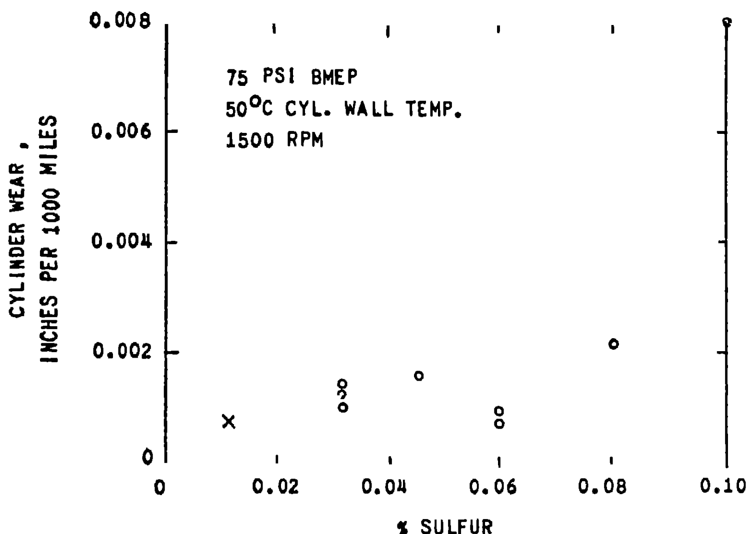


Figure 23. Cylinder Wear in Relation to the Sulfur Content of the Gasoline (Taken from Williams[29])

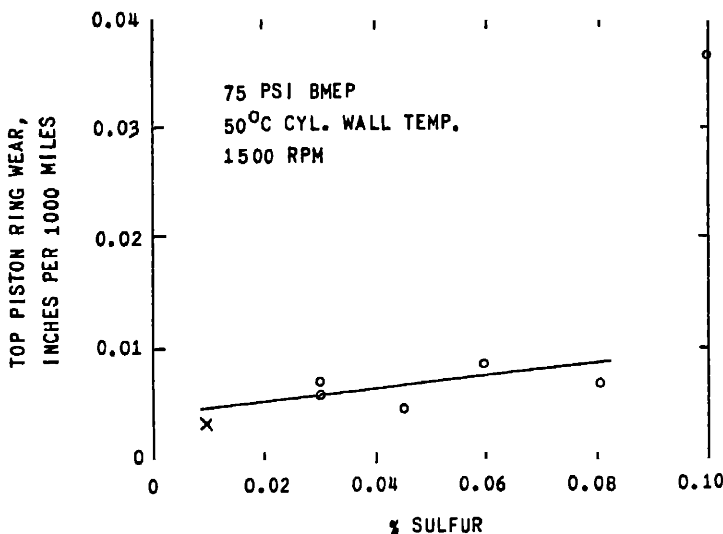


Figure 24. Piston Ring Wear in Relation to the Sulfur Content of the Gasoline. (Taken from Williams[29])

In diesel engines the effect of tetraethyllead fluid is absent, but the effect of sulfur can be quite serious since the average diesel fuel contains much more sulfur than the average gasoline. The effect of

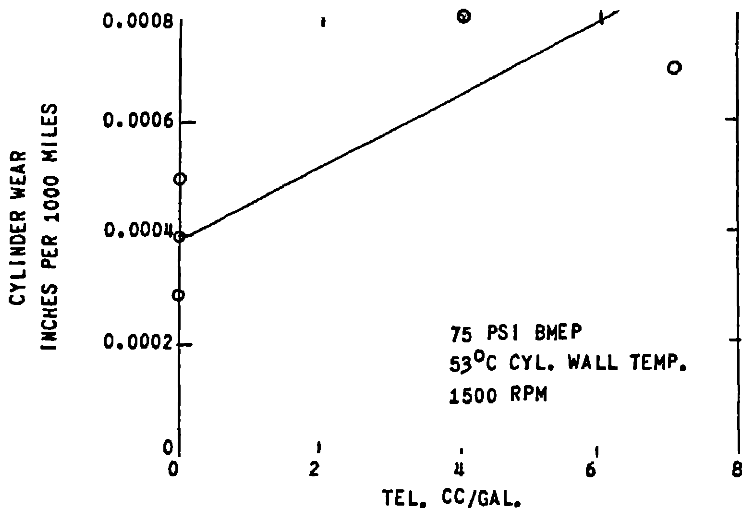


Figure 25. Cylinder Wear in Relation to the Tetraethyllead Content of the Gasoline (Taken from Williams[29])

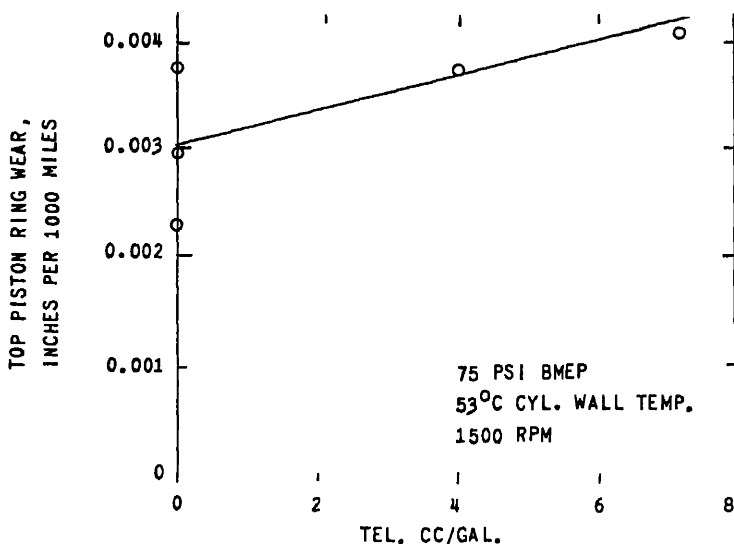


Figure 26. Piston Ring Wear in Relation to the Tetraethyllead Content of the Gasoline. (Taken from Williams[29])

the sulfur content of diesel fuels upon cylinder and ring wear in both high-speed and low-speed diesel engines has been studied by Broeze and Gravesteyn.[9] Their results, which are summarized in

Figures 27 and 28, indicate that sulfur has a definitely detrimental effect in both types of engine. Similar studies have been reported by Cloud and Blackwood,[14] whose conclusions on the effect of sulfur in high-speed engines, as summarized in Figures 29 and 30, are in good agreement with those of Broeze and Gravesteyn. Cloud and

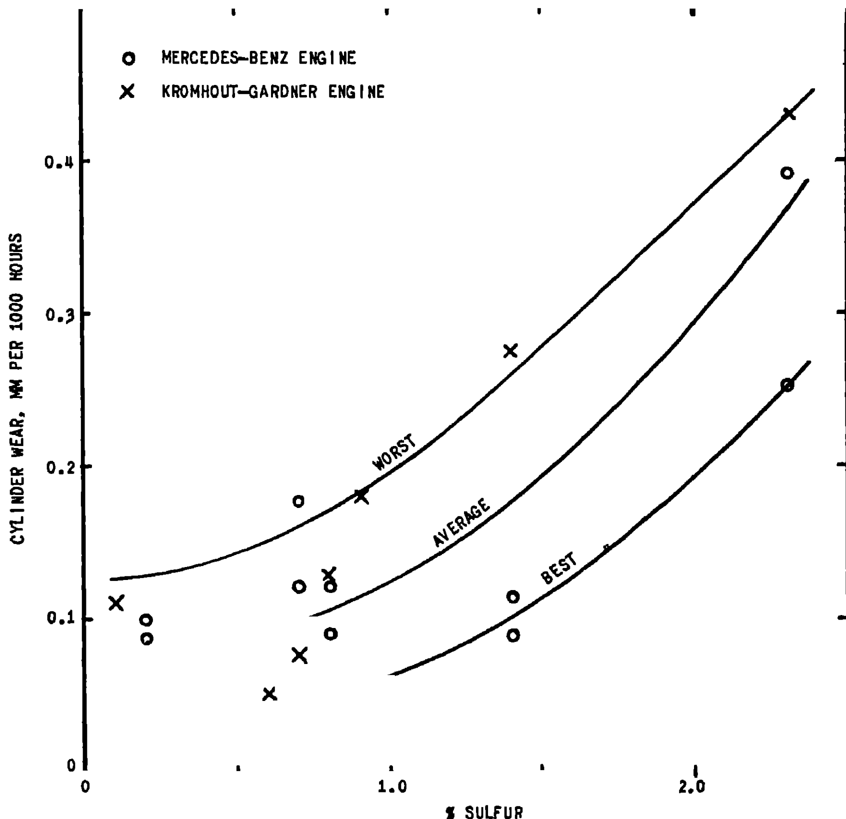


Figure 27 Effect of Sulfur Content of Fuel upon Cylinder Wear in High-speed Diesel Engines (Taken from Broeze and Gravesteyn[9])

Blackwood consider sulfur to be the most important fuel factor affecting wear in high-speed diesel engines. However, their results in low-speed engines differed from those of Broeze and Gravesteyn. The former investigators found no difference in wear from high or low sulfur fuel in this type of engine, while the latter found the effect shown in Figure 28.

The effect of sulfur in high-speed diesel engines was attributed

by Cloud and Blackwood to the presence of sulfur trioxide, since 60 to 90 per cent of the sulfur in the fuel was shown to appear in this form in the exhaust gas. These figures are in qualitative agreement with data reported by the Bureau of Mines,[14] in which it was shown that all the sulfur in a diesel fuel appears in the exhaust gas as sulfur dioxide or sulfur trioxide. The percentage of total sulfur

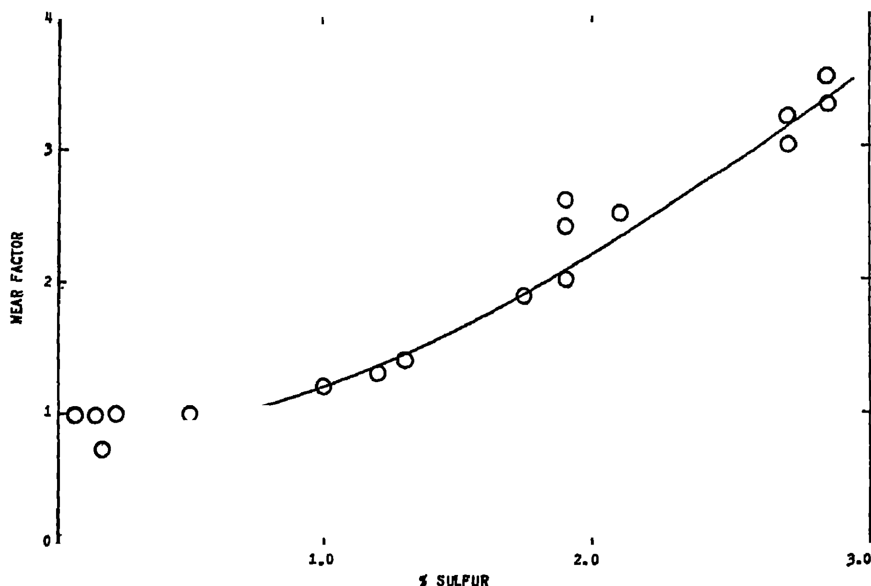


Figure 28 Effect of Sulfur Content of Fuel upon Total Piston and Cylinder Wear in Single Cylinder Low-speed Diesel Engine. (Taken from Broeze and Gravesteyn[9]) (Wear factor = ratio of wear with investigated fuel to wear with reference fuel of 0.7% sulfur.)

appearing as the trioxide varied from 22 to 100 per cent, depending upon operating conditions. The trioxide predominated in most cases. More recent work reported by van der Zijden, van Hinte, and van den Ende[26] indicates that these high values found for sulfur trioxide content may have been in error. It was shown in this work that sulfur dioxide in exhaust gas is readily oxidized to the trioxide during ordinary sampling and analysis When special precautions were taken against oxidation, the sulfur trioxide content of the exhaust gases was found to be of the order of only a few per cent of the total sulfur. It is postulated[26] that the sulfur trioxide and sulfuric acid found

in used engine oils are formed by oxidation of sulfur dioxide in the oil film rather than by direct combustion to the trioxide.

Since sulfuric acid has a much higher boiling point than any of the other acids present in the cylinder after combustion of the fuel, and since corrosive wear is associated with the presence of aqueous

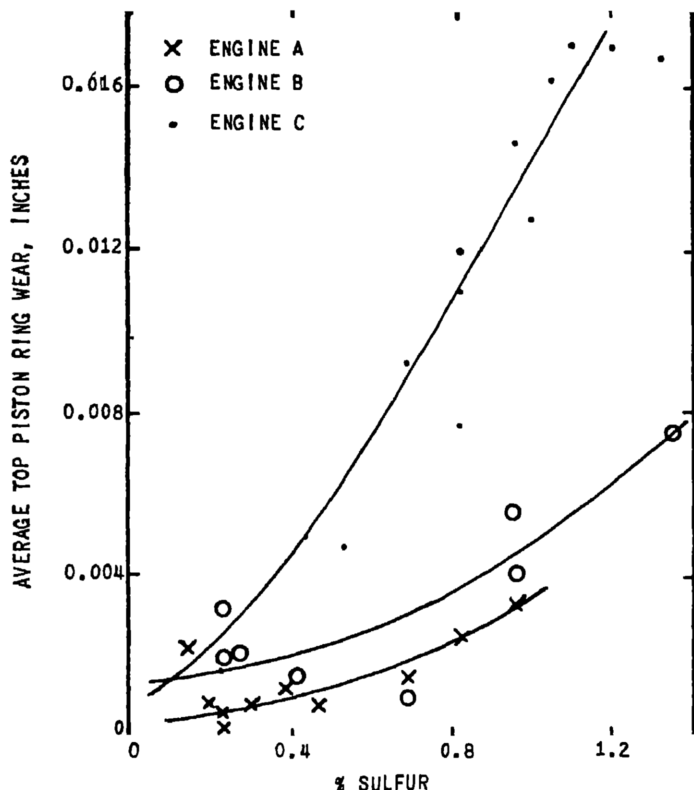


Figure 29 Effect of Sulfur in Diesel Fuel upon Piston Ring Wear. (Taken from Cloud and Blackwood[14])

acids in the liquid state, the presence of sulfur trioxide, and hence sulfuric acid, even in low concentration, would be expected to be particularly detrimental Sulfur trioxide, in the presence of water, not only serves as an acid anhydride which can combine with water to form a corrosive acid, but rasies the dew point as well, so that in effect it broadens the range of temperature and pressure in which corrosion can occur

Alkaline Additives. One solution to the problem of corrosive attack by aqueous acids is the direct one of neutralizing the acids as they are formed. Williams[29] mentioned the possibility of reducing corrosive wear by adding alkaline compounds to the fuel or lubricant, but did not publish any results. Cattaneo and Starkman[12] studied

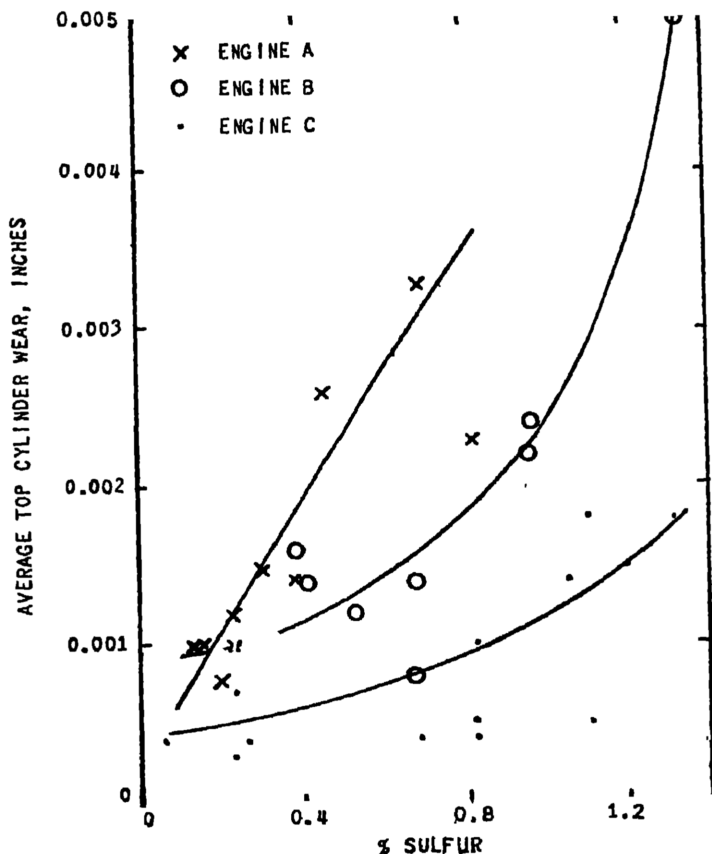


Figure 30. Effect of Sulfur in Diesel Fuel upon Cylinder Wear. (Taken from Cloud and Blackwood[14])

wear in a diesel engine and found that the rate of wear which prevailed when a fuel containing one per cent of sulfur was used could be markedly reduced by the incorporation of suitable organic salts of calcium or sodium added to either the fuel or the lubricant or by lime pellets added to the crankcase. The alkaline compounds added to the fuel or lubricant in low concentration reduced

the rate of wear by 50 per cent or more. The lime pellets were not quite as effective, but showed a significant influence. Cattaneo and Starkman showed, further, that alkaline additives are effective in spark ignition engines as well as in diesels.

Rust Prevention

Machines or machine parts made from ferrous alloys other than stainless steels are subject to rusting unless precautions are taken against exposure to humid air. Mineral oils do not have good antirust properties, although they do offer some protection, and they must be fortified with appropriate additives if any marked degree of rust prevention is to be achieved.

Antirust oils and coatings include the following principal types:

(1) *Oils used in bulk application.* This type includes lubricating oils, e.g., steam turbine oil, which give protection against rusting induced by water which may enter the lubricating system.

(2) *Oil film rust preventives.* Steel surfaces may be protected against rusting for limited periods of time by the application of a suitable oil film, either by dipping or spraying. Rust preventives of this type have the advantage over heavier coatings in that they are more easily removed.

(3) *Semi-solid type coatings.* If steel articles are to be stored for extended periods under severe conditions of humidity or exposed to the action of salt water, it may be necessary to apply a rust-preventive coating of heavier consistency. Such coatings may contain petrolatum, asphalt, or grease. They are usually applied in solution in a light hydrocarbon, which evaporates upon exposure to the atmosphere, or in a molten state at an elevated temperature. They afford a considerable degree of mechanical protection which can be augmented by the incorporation of rust-preventive additives. They are intermediate between oil and paint in ease of removal.

Laboratory tests have been developed for evaluating the rust-preventive characteristics of each of these three types of products. The ASTM[2] has a test for measuring the rust preventive properties of steam turbine oil, which constitutes an important class of antirust oil used in bulk application. This test consists, briefly, of exposing a polished cylindrical steel specimen to an agitated mixture of ten volumes of oil and one volume of distilled water or synthetic sea water. The test is run for 48 hours at 140°F. Undoped mineral oils

permit very rapid rusting in this test, while rust-inhibited turbine oils are required to leave the specimen entirely free from rust.

Oil film rust preventives are commonly tested in a humidity cabinet.[1, 25] A sand-blasted or polished steel specimen is dipped in the oil under test and allowed to drain under prescribed conditions, after which it is exposed to a humidity of 100 per cent at 100°F. Mineral oils allow rusting within a few hours under these conditions. The addition of suitable antirust agents to the oil delays rusting for a period of four hundred hours or more.

Since the semi-solid coatings are intended for use under more severe conditions than those represented by the humidity cabinet test, they are subjected to a more severe test in which a coated steel specimen is exposed to a fog of salt water. This is known as the salt spray test.[24] Specifications for various grades require a protection against rusting for periods varying from a day to a month.

Rust-preventive additives consist of polar compounds which are capable of being adsorbed at the metal-oil interface. As mentioned in Chapter I, compounds which form oleophobic adsorbed films are rust preventives by virtue of the fact that these films are also hydrophobic. Sellei and Lieber[24] have classified rust-preventive additives into the following general types of organic compounds:

(1) Esters, e.g., sorbitan monooleate, butyl stearate, butyl naphthenate.

(2) Nitrogen compounds, e.g., amines and amides.

(3) Phosphorus compounds, e.g., esters of phosphorus acids.

(4) Metal soaps, e.g., aluminum stearate.

(5) Carboxylic acids, e.g., the dicarboxylic acids made by reacting olefins with maleic anhydride.

Most of these compounds are effective as rust preventives because of their polarity, although some, notably the amines, may function partially through their ability to neutralize free acidity. Barnum, Larsen, and Wachter[8] studied the adsorption of polar additives from mineral oil solution. The adsorbent they used was iron powder of known surface area They found that good rust inhibitors are strongly adsorbed as multilayers rather than monomolecular films. Additives which were weakly adsorbed were ineffective as rust preventives.

Pilz and Farley[22] studied the mechanism of rust prevention and found that strength and extent of orientation at the metal-oil in-

terface is indicated, indirectly, by the extent to which water spreads on the oil. The contact angle formed by a droplet of water on an oil film is therefore a measure of the rust preventive properties of the oil. Oils upon which water formed a contact angle of 70° or greater were found to permit rusting within 24 hours in the humidity cabinet. Those which showed angles of 5 to 10°, on the other hand, did not allow rusting until about 400 hours had elapsed. Oils of intermediate contact angles gave intermediate performance in the humidity cabinet. Pilz and Farley point out the fact that the contact angle method for evaluating rust preventives must be used with discretion, since the correlation with life in the humidity cabinet fails when the polar additive present is readily leached from the oil by water or when the additive is present in excessive concentration (greater than about 10 per cent).

Bibliography

1. Army-Navy Aeronautical Specification AN-H-31, April 2, 1945, on Operation of Humidity Cabinets.
2. A S T.M. Designation D665-47T, "Tentative Method of Test for Rust Preventing Characteristics of Steam Turbine Oil in Presence of Water."
3. Barnum, E R , Larsen, R. G , and Wachter, A., paper presented before National Association of Corrosion Engineers, St. Louis, April, 1948.
4. Beeck, O , *J. Applied Phys.*, **12**, 512–18 (1941).
5. Beeck, O , Givens, J W., Smith, A E , and Williams, E C., "Proceedings of Special Conferences on Friction and Surface Finish," pp. 112–21, Cambridge, Mass , Mass Inst Technol., June, 1940
6. Beeck, O , Givens, J W., and Williams, E. C , *Proc. Roy. Soc (London)*, **A177**, 103–18 (1940)
7. Berger, L B., Elliott, M. A , Holtz, J. C., and Schrenck, H. H., *U. S Bur. Mines*, Report of Investigation 3713 (1943)
8. Boerlage, G D , and Gravesteyn, B J. J , *The British Motorship*, **13**, 171–3 (1932).
9. Broeze, J J , and Gravesteyn, B. J. J , *The British Motorship*, **19**, 408–14 (1938).
10. Bruce, C S., Duck, J T , and Pierce, A R., *J Research Natl. Bur. Standards*, **41**, 135–49 (1948)
11. Burwell, J T , Kaye, J , and van Nymegen, D. W., "Proceedings of Special Conferences on Friction and Surface Finish," pp 266–11, Cambridge, Mass., Mass. Inst Technol , June, 1940
12. Cattaneo, A G , and Starkman, E. S , paper presented before Special Summer Conference on Mechanical Wear," Mass Inst Technol , Cambridge, Mass. June, 1948.
13. Clark, G L , Sterrett, R R , and Lincoln, B H , *Ind. Eng Chem* , **28**, 1326–8 (1936).
14. Cloud, G H , and Blackwood, A. J., *S A E Journal*, **51**, 408–14 (1943).
15. Davis, L L , Sibley, B E , and Lincoln, B H , *Refiner Natural Gasoline Mfr.*, **14**, 523–36 (1935).

16. Dayton, R. W , "Proceedings of Special Conferences on Friction and Surface Finish," pp 127–40, Cambridge, Mass. Mass Inst. Technol., June, 1940.
17. Everett, H. A., *S.A.E. Journal*, **51**, 165–9 (1943).
18. Everett, H. A., and Keller, G. H., *Inst. Mech. Engrs* , "General Discussion on Lubrication," Vol. I, pp. 451–6, 1937.
19. Finch, G. I., and Zahoorbux, F D., *Inst. Mech. Engrs.*, Vol. II, pp. 295–301, 1937.
20. Larsen, R. G., and Perry, G. L., *Trans. Am. Soc. Mech. Engrs.*, **67**, 45–50 (1945).
21. Neely, G L., *Inst Mech Engrs* , "General Discussion on Lubrication," Vol. II, pp 378–85, 1937.
22. Pilz, G. P., and Farley, F. F., *Ind. Eng. Chem.*, **38**, 601–9 (1946).
22a. Pinotti, P. L., Hull, D. E., and McLaughlın E J., *Petroleum Engr.*, **21**, (6), 2–5 (1949).
23. Poppinga, R., "Wear and Lubrication of Piston Rings and Cylinders," Berlin, 1942 (English translation by E. Kurtz published by Am. Soc. Lubrication Engrs)
24. Sellei, Helen, and Lieber, Eugene, *Lubrication Eng.*, **3**, 16–23, 42, Sept.,1947.
25. Todd, Floyd, *Ind. Eng. Chem., Anal. Ed.*, **16**, 394–7 (1944).
26. van der Zıjden, M. J., van Hinte, J. E., and van den Ende, J. C., *J. Inst. Petroleum*, **36**, 561–74 (1950).
27. Wallace, D. A., "Proceedings of Special Conferences on Friction and Surface Finish,' pp. 22–43, Cambridge, Mass., Mass. Inst. Technol., June, 1940.
28. Williams, C G., *Inst. Mech. Engrs.*, "General Discussion on Lubricatıon," Vol. I, pp. 588–94, 1937.
29. Williams, C. G , *Inst Automobile Engrs.*, "Collected Researches on Cylinder Wear," 1940.

Chapter VIII
MANUFACTURING METHODS

Introduction

The world-wide production of lubricating oil in 1948 averaged 169,000 barrels per day. All but 18,000 barrels per day was manufactured in the United States.[15b] Fractions derived from petroleum are the major components of most lubricating oils. In many instances they serve as the sole components, although the trend is toward the incorporation of one or more specific addition agents or "additives". These addition agents are usually synthetic organic compounds.

Lubricants other than mineral oils are sometimes used. These are in some instances synthetic compounds and in others naturally occurring products obtained from a source other than petroleum. Since petroleum lubricants are relatively inexpensive, the nonpetroleum products find a use only where petroleum is scarce or in special applications where certain properties, e.g., very low pour point and very flat viscosity-temperature curve, are desired which are either lacking or present in insufficient degree in mineral oils.

Composition of Mineral Oil Base Stocks

Crude petroleum consists of a very complex mixture of hydrocarbons plus minor amounts of other organic compounds, chiefly those containing oxygen, sulfur, or nitrogen. The hydrocarbons vary in molecular size from methane to compounds of such high molecular weight and low volatility that they cannot be distilled even under high vacuum. They vary in structure from normal paraffins to condensed-ring aromatics with alkyl side-chains. The distribution of the various molecular sizes and types, and hence the amount of potential lubricating oil present in a given crude oil, varies widely with the source of the crude. Some crudes consist predominantly of gasoline and naphthas and others contain asphalt as the principal constituent. Still others contain lubricating oil distillate and residue as major components, together with gasoline, naphthas, gas oil, wax, and asphalt in varying percentages.

The Bureau of Mines has worked out a routine method for analyzing crude oil.[70, 83] It consists of the determination of specific gravity, viscosity, and sulfur, and a distillation. The latter is started at atmospheric pressure. Cuts are taken at 25°C intervals from 50 to 275°C. The distillation is then continued at a pressure of 40 mm of mercury and cuts are taken at 25°C intervals from 200 to 300°C. Volume and specific gravity are determined on all fractions and on the residuum. Viscosity is determined on the distillate samples taken at 40 mm pressure. Fractions boiling below 200°C at atmospheric pressure and having specific gravities of 40° API (specific gravity 0.825) or lighter are classified as "gasoline and naphthas." Fractions boiling between 200 and 275°C and having gravities of 40° API or lighter are classified as "kerosene". Fractions heavier than 40° API and with a viscosity less than 50 seconds Saybolt Universal at 100°F are termed "gas oil" distillate. Fractions more viscous than 50 seconds Saybolt at 100°F are defined as "lubricating oil distillate."

Analysis of 215 selected samples of representative crude oils, all from the United States, shows sulfur content ranging from less than 0.17 per cent to more than 4 per cent; gasoline and naphtha from 0 to 90.4 per cent; kerosene from 0 to 25.0 per cent; gas oil from 0 to 50.7 per cent; lubricating oil distillate from 0 to 39.2 per cent; and residuum from 1.2 per cent to 53 7 per cent.[83]

The high molecular weight and complexity of lubricating oil make separation into pure compounds virtually impossible. Rossini and his coworkers[25] at the National Bureau of Standards have made an extensive study of the composition of the lubricating oil fraction of a Mid-Continent crude. This particular sample contained 14.5 per cent lubricating oil distillate and 12.7 per cent residuum by the Bureau of Mines method. Sixteen narrow distillate fractions in the lubricating oil range, constituting 10 per cent of the crude, were used in this study. Separations were made by various physical means including fractional distillation under high vacuum, crystallization (dewaxing), liquid-liquid extraction, and adsorption on silica gel. The individual fractions were then analyzed. It was concluded that this particular lubricating oil fraction contained the following distribution of molecules:

(1) 43–51 per cent of 1, 2, or 3 naphthenic rings with paraffinic side chains.

(2) 8.3 per cent of 1, 2, or 3 naphthenic rings and 1 aromatic ring with paraffinic side chains.

(3) 8.1 per cent of 2 naphthenic rings and 2 condensed aromatic rings with paraffinic side chains.

(4) 6.6 per cent of 1 naphthenic ring and 3 condensed aromatic rings with paraffinic side chains.

(5) 18 to 20 per cent of normal paraffins plus possibly some isoparaffins.

(6) 8 per cent asphaltic constituents.

The absence of isoparaffins is somewhat surprising in view of the fact that this class of hydrocarbon does occur in the lighter fractions of petroleum, e g., gasoline. It has been confirmed by Müller and Neyman-Pilat,[22] who made a study of the composition of two paraffinic lubricating oils, one of Pennsylvanian and the other of Polish origin. Both of these oils were shown to be virtually free from isoparaffins. Crude petroleum from other sources may, of course, contain this type of hydrocarbon.

Vlugter, Waterman, and van Westen[35] have worked out an analytical method, often referred to as the Waterman analysis, for determining the concentration of aromatic rings, naphthenic rings, and paraffins (free paraffins and paraffinic side-chains) in petroleum fractions in the lubricating oil range. Originally the method consisted of a determination of aromatics by a quantitative catalytic hydrogenation and a subsequent determination of paraffins in the hydrogenated oil from the molecular weight and the specific refraction. Aromatics were calculated from the quantity of hydrogen consumed and the naphthenes initially present were determined by difference. It was subsequently found that the specific refraction of the hydrogenated oil could be predicted from the properties of the original oil and its aniline point * The latter value, together with molecular weight, also permits the calculation of aromatic content. Thus the distribution of aromatic rings, naphthene rings, and paraffins or paraffinic side chains can be calculated from the following experimentally determined physical constants: (1) density, (2) refractive index, (3) molecular weight, (4) aniline point.

* Lowest temperature at which a mixture of equal volumes of aniline and sample form a single phase

Refining

The refining of lubricating oil usually involves several steps, each designed to remove certain undesirable components. Some refining methods are chemical, while others are purely physical. The physical methods include distillation, solvent precipitation, solvent extraction, crystallization, and adsorption. Of the chemical methods of refining, treatment with sulfuric acid is by far the most common. Others include hydrogenation and treatment with aluminum chloride.

Distillation. Distillation is commonly employed to remove components which are of too low molecular weight to be included in lubricating oil. The presence of such components reduces the viscosity and the flash point. Another purpose of distillation is to separate lubricating oil fractions into narrower fractions in order to provide products of varying viscosity grades. Both distillate fractions and residues are used as lubricants. In addition, distillation is often used to separate lubricating oil from asphaltic constituents, which must be removed to avoid interference in subsequent refining steps. In this operation the distillate is converted into lubricating oils and the residue into asphalt.

Except for certain very light grades, lubricating oil cannot be distilled at atmospheric pressure, for the boiling ranges correspond to temperatures at which cracking occurs at an appreciable rate. Cracking during distillation is highly undesirable, not only because it converts potential lubricating oil to more volatile and less valuable products, but because of the adverse effect the presence of small concentrations of cracked material has upon the quality, notably oxidation stability, of the lubricating oil. In the commercial distillation of lubricating oil the temperature is kept at as low a level as practical by the use of vacuum or steam or both. Some cracking may occur even under these conditions. Brown and Tannich[6] showed that lubricating oil made in the laboratory by distillation under high vacuum and at a low temperature in a "molecular still" is much more stable toward discoloration in storage than that produced from the same starting material in plant distillation. They attribute the greater stability of the laboratory product to the absence of decomposition products formed by severe distillation.

Solvent Precipitation or Deasphalting. High molecular weight components of a resinous and asphaltic nature cannot be tolerated

in a finished lubricating oil, since they cause excessive sludging in service. They also have a serious adverse effect upon color and carbon residue. As mentioned above, these components may be removed by distillation, in which case the distillate fractions, or "neutrals", are used as lubricating oil and the residue is used as a component of asphalt. This method of deasphalting has the disadvantage that it does not produce a residual lubricating oil, or "bright stock". Bright stocks are valuable and necessary components in the heavier grades of lubricating oil.

When a mixture of lubricating oil and asphalt is diluted with a light hydrocarbon such as propane at room temperature or higher, a phase separation occurs.[16, 8] Oil and any wax present in the oil remain dissolved in the propane, which is liquid at the pressure employed, while the heavier asphalt and resins precipitate in the form of a viscous liquid. The separation is primarily according to molecular size rather than type. The two layers, which separate quite readily, are led to separate distillation systems for the removal of propane and the production of bright stock and asphalt.

Solvent Extraction.[3, 16, 21, 31, 38] After resins and asphalt are removed, the remaining oil is in general still not satisfactory as a lubricant. Most crudes contain sufficient aromatics in the lubricating oil range to cause excessive sludging and carbonization during high temperature operation and to affect the viscosity-temperature slope adversely. Furthermore, most oils contain wax, which seriously affects the low temperature flow characteristics of the oil. Thus, further refining steps are necessary.

If the oil, which consists of paraffinic, naphthenic, and aromatic constituents, is mixed with an appropriate polar solvent, a phase separation can be effected. The paraffinic and naphthenic constituents concentrate in the upper, or raffinate, phase, and the aromatic constituents in the lower, or extract, phase. The solvent, while present in both phases, is concentrated in the lower. In plant practice several stages of extraction are normally used, either through multiple batch operation or through counter-current flow in multiple chambers or in packed towers. The separated phases are subjected to distillation in separate systems for the recovery of solvent and the production of raffinate (extracted oil) and extract.

Extraction with liquid sulfur dioxide (Edeleanu process) is the oldest solvent refining method in the petroleum industry. It is

particularly well-suited for the extraction of light distillates. The Duo-Sol, the furfural, and the phenol processes constitute the principal extraction methods in general commercial use in the refining of lubricating oils. The Duo-Sol process, as the name implies, uses two solvents, namely, propane and mixed cresols. It is peculiarly suitable for refining residual oils containing asphalt. Such oils can be processed directly without a preliminary deasphalting step. The process can be used for extracting distillate oils as well.

A convenient and useful physical property for following the course of solvent extraction is the specific dispersion,[36] which is defined as the difference in specific refraction for two spectral lines The specific dispersion for all paraffins and naphthenes is approximately the same, whereas it is much higher for aromatics The value, in the case of aromatics, increases with the number of aromatic rings in the molecule. Molecules containing both aromatic and naphthenic and/or paraffinic groups have intermediate values. Lubricating oils produced from different crudes but extracted to a constant aromatic content have specific dispersion values which are approximately equal, while other properties which are sometimes used to follow the course of extraction, such as viscosity index, refractive index, and aniline point, show a considerable spread, since they vary with molecular weight and/or paraffin-naphthene ratio as well as with aromatic content.

Crystallization or Dewaxing.[16] Wax, which consists of a mixture or normal paraffins and other hydrocarbons of high melting point and low solubility in oil at low temperatures, interferes with the flow of a lubricant at low temperatures. It cannot, therefore, be tolerated except in low concentration in a finished lubricant unless the oil is to be used under conditions in which low temperatures are not encountered, e.g., indoors or in tropical climates.

Dewaxing processes consist of chilling to effect a separation of the wax. An oil can be dewaxed simply by chilling to bring about a phase separation, followed by removal of precipitated wax, usually by means of a filter press. This process is still used commercially for processing light fractions. The commercial trend, however, is toward solvent dewaxing, in which the oil is diluted prior to chilling. Dilution renders the mixture less viscous at the temperatures employed, which are in the region of −20°F, and reduces entrainment of oil in the wax cake in the subsequent filtration or centrifuging step,

thus enhancing the yield of dewaxed oil. The solvent is chosen on the basis of its low solvency for wax and high solvency for oil, as well as factors of economic importance such as initial cost and ease of distillation for the recovery of solvent. Propane and mixtures of methyl ethyl ketone and benzene find preponderant commercial use. Ethylene chloride, trichloroethylene, and naphtha are used to a lesser extent.

The pour point of the dewaxed oil is determined by the conditions of dewaxing, notably the temperature and solvent used. Dewaxing to an extremely low pour point is not justified except in special instances, since very low temperatures must be used and since the loss in yield of oil is high. The viscosity-temperature slope of the dewaxed product is normally steeper than that of the raw oil, since wax has a relatively flat viscosity-temperature curve. This factor is an additional reason for dewaxing only as deeply as necessary.

Treatment with Chemical Reagents.[17] Sulfuric acid treatment is one of the oldest processes in the petroleum industry. It consists, briefly, of agitating the oil with concentrated sulfuric acid, separating the oil from the acid sludge by settling or centrifuging, and finally removing oil-soluble acid reaction products by washing with aqueous caustic soda or by adsorption on clay. In the case of highly viscous oils, dilution with naphtha or propane may be used to facilitate sludge separation.

The action of sulfuric acid is both physical and chemical, although the latter effects usually predominate. The components removed by sulfuric acid are in general the same as those removed by solvent extraction. Since solvent extraction offers many operational advantages over acid treatment, it has to a large degree supplanted the older method of refining.

Aluminum chloride may be used in place of sulfuric acid for treating lubricating oil.[16] Its commercial use, compared to that of sulfuric acid, is limited.

Adsorption. When an oil is treated with an adsorptive solid, certain impurities are removed.[17] The adsorbent may be applied either by means of percolation, in which the oil, preheated to the extent necessary for adequate flow, is passed slowly through a tower filled with granular adsorbent; or by a "contact" method, in which a more finely divided adsorbent is agitated with the oil and then removed by filtration. Various clays, either in their natural state or

treated chemically, are commonly used as adsorbents, although others may be employed. Clay used in the percolation method is easily regenerated by burning. Spent contact clays do not lend themselves to ready recovery and are generally discarded.

Impurities most likely to be removed by this type of treatment include suspended solids, which are removed by simple filtration, and suspended water droplets and dissolved polar ingredients such as naphthenic acid, phenols, soaps, etc., which are removed by adsorption. As far as properties of the finished oil are concerned, the main effect of clay treatment is to improve the clarity and color, although there may be a distinct effect upon oxidation stability. There is little effect upon the hydrocarbon composition of the product. If large amounts of adsorbent were used it would be possible to effect a major change in composition through selective adsorption of additional polar constituents and aromatics. However, solvent extraction is a more practical way of accomplishing this end, and clay treatment is normally used only as a finishing step to remove traces of undesirable constituents either present in the oil originally or formed in a previous refining step.

Hydrogenation.[28c] Lubricating oil consists essentially of a mixture of paraffinic and naphthenic hydrocarbons. It would therefore appear from theoretical grounds that fractions unsatisfactory as lubricants because of too high an aromatic content or the presence of polar impurities could be improved by hydrogenation and that the yield should be high.

Hydrogenated oils of good quality and high yield have been prepared from inferior lubricating oil distillates.[9, 14a] A serious disadvantage of hydrogenation is the decrease in viscosity that is effected, particularly in the case of the heavier fractions.[21b] Moreover, the process cannot compete economically with solvent extraction or acid treatment, and it is not used commercially except for some synthetic products.

Blending. The last step in the manufacture of lubricating oil is the blending of base stocks to meet viscosity requirements and the incorporation of specific additives. Additives are normally used in low concentration—from a fraction of a per cent to five per cent. Their function may be one or more of the following: (1) improve lubricity under "boundary" conditions; (2) impart extreme pressure characteristics; (3) reduce pour point; (4) improve viscosity-tempera-

ture relationship (raise Viscosity Index); (5) inhibit oxidation; (6) combat catalytic effect of metals and contaminants; (7) reduce bearing corrosion; (8) disperse sludge particles, thus helping to maintain clean engine; (9) cause emulsification (e.g., soluble cutting oils); (10) reduce or eliminate foaming; (11) reduce or eliminate rusting; and (12) reduce ring and cylinder wear. The functions of these various additives are discussed in earlier chapters.

In the case of oils the process of blending consists merely of mixing, since the final product is a homogeneous solution. The manufacture of greases, which consist of soap colloidally dispersed in oil in the form of a gel, is a much more complicated process.[19] Most greases contain either sodium or calcium soaps, although soaps of aluminum, lead, lithium, barium and other metals are used. They vary in properties from semifluid products containing a few per cent of soap to hard block greases containing roughly equal proportions of oil and soap. Since greases are colloidal systems, their properties are determined not only by their basic composition but also by the structure of the colloidal soap particles, which is in turn influenced by such factors as manner of mixing, rate of cooling, etc.

Nonpetroleum Lubricants

Nonpetroleum lubricants vary from low-grade substitutes, used particularly in war-time conditions because nothing else is available, to high-grade, "tailor made" products for highly specialized applications.[21a] During World War II the following were used as substitute lubricants in France:[32] molasses and its dehydration residue for transmissions, 2 per cent dextrose solutions as soluble oils, polymerized anthracene and solutions of orthosilicates for various purposes, and a mixture of sea-mud and potassium soaps as axle grease. Vegetable oils, including olive, rapeseed, castor, and cottonseed oils may be used as crankcase lubricants but are inferior to mineral oils with respect to the deposition of sludge and lacquer.[1, 4, 34]

Synthetic Hydrocarbons. The amount of research that has been done on synthetic oils is illustrated in a bibliography published in 1945 which lists 205 literature references and 370 patents.[37] Many additional papers and patents have appeared since the compilation of that bibliography.

The polymerization of olefins constitutes one of the most widely

studied means of synthesizing lubricating oil. Sullivan, Voorhees, Neeley, and Shankland[30] have prepared lubricating oil by the polymerization of various olefins with aluminum chloride as catalyst. They found that products made from straight-chain olefins of high molecular weight, e.g., cetene or cracked wax olefins, had much flatter viscosity-temperature curves (higher Viscosity Index) than those made from branched olefins or those of low molecular weight, e.g., trimethyl ethylene, ethylene. Cyclic olefins, e g., turpentine, give products of very low Viscosity Index. These results are consistent with the known effects of structure of viscosity-temperature relationships which are discussed in Chapter II, i.e., steep viscosity-temperature curves are associated with cyclic or highly branched structures whereas flat curves are associated with long paraffinic chains.

Lubricating oils made by the polymerization of olefins do not form insoluble oxidation products (sludge) when heated in the presence of air.[30] This is because they do not contain aromatics.* The oxidation products are of an acidic nature and are soluble in the oil. The stability of olefin polymers against acid-formation may be increased by hydrogenation.[12, 29]

Synthetic oils of the olefin-polymer type may be made from coal by utilizing the Fischer-Tropsch process[10, 11, 12] in which carbon monoxide and hydrogen, which are produced from coal via the water-gas reaction, are converted to a mixture of olefinic and paraffinic hydrocarbons. Lubricating oils may be made by polymerizing these olefins Aluminum chloride or other metal halides are usually employed as catalyst in this reaction. Other catalysts include sulfuric acid and clay. The reaction can even be accomplished in the absence of catalyst by using electrical charges of high voltage and high frequency (the Voltol process), alpha or beta rays, x-rays, ultraviolet rays, or heat and pressure.[30]

Synthetic oil may also be made by reacting an olefin with an aromatic. This may be accomplished by chlorinating the olefin, e.g., a Fischer-Tropsch "gas-oil", or "Kogasin", and allowing the chlorinated olefin to react with an aromatic, e.g., xylene, by the Friedel-Crafts reaction.[10] Coke oven tar and coke oven gas have been mentioned as starting materials in the manufacture of lubricating

* The effect of composition of an oil upon the nature of its oxidation products is discussed in Chapter III.

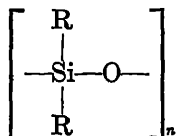
oils of this type.[15] Products made by alkylating condensed ring aromatics such as naphthalene, phenanthrene, fluorene, pyrene, chrysene, and anthracene with an alpha olefin, e.g., 1-heptene or 1-dodecene, have also been claimed to be stable lubricants.[7]

The manufacture of synthetic oils was of vital importance to the German war effort in World War II.[15a, 23a] Approximately one tenth of the lubricating oil produced in Germany during that period was made synthetically. Half of the synthetic oil produced was for aviation use, and the volumes of synthetic lubricant and petroleum oil used in aviation were approximately equal. Most of the synthetic oil for this use was made by the polymerization of olefins. One of the larger plants used ethylene as a starting material and the others used higher olefins produced by cracking Fischer Tropsch gas oil, or wax or natural wax, or sweat oil obtained in wax manufacture. The German olefin polymer lubricants had certain outstanding properties. Most of them had Viscosity Index values greater than 100 and pour points well below 0°F. One ethylene polymer was reported to have a Viscosity Index greater than 140 and a pour point lower than −100°F.[15a] Murphy and Saunders[23a] made a thorough analysis and study of three different viscosity grades of German polyethylene oils. The lightest grade had a Viscosity Index of 96 and a pour point of −85°F. The heavier grades had Viscosity Index values of about 110 and pour points of −10 and −20°F. Ultraviolet and infrared absorption spectra analysis of the oils indicated that they are chain-like hydrocarbons with occasional double bonds and with a few branched chains, most of which are methyl groups. Oxidation studies and engine tests showed the oxidation stability to be poor in comparison to that of petroleum lubricants. This is not surprising in view of the effect of olefinic unsaturation on oxidation stability indicated in Chapter III. However, the polyethylene oils showed a good response to certain antioxidants.

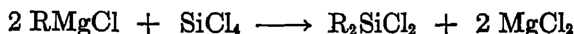
Synthetic Nonhydrocarbons. In addition to the synthetic hydrocarbon lubricants described above, four different types of nonhydrocarbon lubricants have been developed in recent years. These are silicones, polyalkylene glycols, diesters, and fluorocarbons. All are more expensive than mineral oils, but for special applications the added cost is often justified.

Silicones[7a, 7b, 18, 23, 23b, 24] The silicones derive their name from the similarity between their empirical formula, R_2SiO, to that of

ketones. Actually the structures of silicones and ketones differ markedly. The latter are simple molecules, $R—\overset{\overset{\displaystyle O}{\|}}{C}—R$; the former are polymers,



Silicones may be made by the hydrolysis of dialkyl dichloro silanes, $SiCl_2R_2$, which are in turn made either through the Grignard reaction:



$$2\,RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2\,MgCl_2$$

or by the direct action of silicon on an alkyl halide:



$$SiO_2 + 2C \longrightarrow Si + 2CO$$



$$Si + 2RCl \longrightarrow R_2SiCl_2$$

Properties of the polymer may be varied by changing the R group or by changing the chain length. The commercially available silicones have been classified into the following four groups according to their properties: varnishes and resins, rubbers, greases, and fluids.

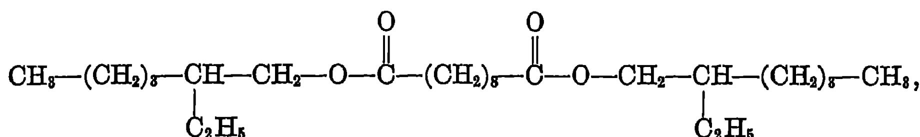
The silicones are, in general, characterized by a high stability and low volatility. The fluids have low freezing points and very flat viscosity temperature curves. They are virtually insoluble in mineral oil. They are used as hydraulic fluids and liquid dielectrics. Both the heavy fluids and the greases are used as lubricants for special applications. The greases, in addition to having the characteristics mentioned above, retain their grease structure over a wide temperature range.

Polyalkylene Glycols [20, 21c, 23, 26, 27] The polyalkylene glycols have several unique properties which recommend them as lubricating oil. They have viscosity-temperature curves which, while considerably steeper than those of the silicones, are flatter than those of mineral oils. They are only partially miscible with most mineral oils at room temperatures, but become completely miscible at elevated temperatures.

Polyalkylene glycols are claimed to form volatile oxidation products rather than insoluble sludge and to have the ability to dissolve

or peptize sludge formed by the oxidation of hydrocarbons. Internal combustion engines operated on these lubricants should, therefore, remain relatively free from deposits, since no deposits are formed by the lubricant and since sludge formed by the fuel remains dissolved or suspended in the oil. Polyalkylene glycols exhibit good cold-starting characteristics since they have low pour points and relatively low viscosities at low temperatures.

Diesters.[2, 5, 12a, 13, 28] A large number of esters of dibasic acids, e.g., phthalic, adipic, and sebacic, have been examined as light lubricating oil. Di-2-ethyl hexyl sebacate,



is probably the best-known member of this class. It has a viscosity temperature slope comparable to those of the polyalkylene glycols. It has a very low freezing point and a low volatility. Its viscosity is that of a very light lubricating oil. This combination of properties makes this compound well suited for use as an instrument oil, e.g., for use in aircraft.

Diesters were used extensively as gun oils, aviation hydraulic fluids, etc., by the Germans during World War II.[15a] Since sebacic acid was not available, the diesters were manufactured from adipic and methyl adipic acids, made from phenol and cresol, respectively. The alcohols used included cyclohexanol, *p*-methyl cyclohexanol, and a mixture known as isobutyl oils which consisted of branched-chain alcohols from C_8 to C_{14} and which was obtained from the methanol synthesis.

Unlike the silicones and the polyalkylene glycols, the diesters are in general completely miscible with mineral oils and may be blended with them if intermediate properties are desired.

Fluorocarbons.[14, 23, 28] Fluorocarbons can be made by fluorinating hydrocarbons in the liquid phase with silver fluoride[28] Their outstanding characteristic is their extreme stability. They are therefore suitable for applications involving very high temperatures. They cannot be used to good advantage over a wide temperature range, for their viscosity-temperature curves are exceedingly steep—much more so than those of lubricating oil of low Viscosity Index

Bibliography

1. Aggarwal, J. S., and Verman, L. C , *Bull Indian Ind Research Bur* , No. 18, Pt. I., 5-25 (1940); *Chem. Abstracts*, **36**, 5994 (1942).
2. Atkins, C. D., Jr., Baker, H. R., Murphy, C. M , and Zisman, W. A , *Ind. Eng. Chem.*, **39**, 491–7 (1947).
3. Auld, S J. M., *J. Inst. Petroleum Technol.*, **22**, 57–77 (1936).
4 Balada, A , *Petroleum Z.*, **33**, No 38, 1–8, No. 40, 1–8 (1937); *Chem. Abstracts*, **32**, 3943 (1939).
5. Bried, E. M., Kidder, H F., Murphy, C. M , and Zisman, W. A., *Ind Eng. Chem.*, **39**, 484–91 (1947).
6. Brown, O. A., and Tannich, R. A , *Oil Gas J* , **36**, No. 46, 80–2 (1938).
7. Cagniant, P., Deluzarche, A., and Colomb, M , *Ann Mines*, **134**, 456–72 (1945; *Chem. Abstracts*, **40**, 2286 (1946)
7a Currie, C. C., and Hommel, M. C , *Ind. Eng. Chem* , **42**, 2452–6 (1950)
7b. Currie, C. C , and Smith, B F., *Ind Eng. Chem* , **42**, 2457–62 (1950).
7c. Dean, E. W , Hill, H. H , Smith, N. A C., and Jacobs, W A., *U. S. Bur. Mines Bull* , No. 207, (1922)
8. Dickinson, J T., and Adams, N. R., *Oil Gas J.*, **44**, No. 47, 185-200 (1946).
9. Ellis, C , "Hydrogenation of Organic Substances", p 579, New York, D. Van Nostrand Co., 1930.
10. Fischer, F., and Koch, H , *Brennstoff Chem.*, **14**, 463–8 (1933); *Petroleum Refiner*, **23**, 260–6 (1944).
11. Fischer, F., Koch, H., and Wiedeking, K , (translated by E. J. Barth) *Petroleum Refiner*, **23**, 312–16 (1944).
12 Gall, D., *J Soc. Chem. Ind.*, **65**, 185–9 (1946).
12a Glavis, F L., *Ind. Eng Chem* , **42**, 2441–6 (1950).
13. Glavis, F. L , and Stringer, H R , A S.T M. Special Technical Publication No 77, Symposium on Synthetic Lubricants (1947).
14. Grosse, A. V., and Cady, G. H., *Ind Eng. Chem.*, **39**, 367–74 (1947)
14a Haslam, R T., and Bauer, W C , *S.A.E Journal*, **28**, 307–12 (1931).
15. Ivanov, K I., and Blagova, T A , *J. Applied Chem U S S.R* , **18**, 158–71 (1945); *Chem. Abstracts*, **39**, 5443 (1945).
15a. Horne, W. A , *Ind Eng. Chem.*, **42**, 2428–36 (1950)
15b Keyser, P. V , *Petroleum Processing*, **4**, 1091–3 (1949).
16. Kalichevsky, V. A., "Modern Methods of Refining Lubricating Oil", New York, Reinhold Publishing Corp , 1938.
17. Kalichevsky, V. A., and Stagner, B. A., "Chemical Refining of Petroleum", New York, Chemical Catalog Co., Inc (Reinhold Publishing Corp), 1933
18. Kauppi, T A., and Pedersen, W W., *Lubrication Eng.*, **2**, 158–61 (1946), *ibid* , **3**, 17–19 (1947).
19. Klemgard, E. N., "Lubricating Greases", New York, Reinhold Publishing Corp., 1937.
20. Kratzer, J C , Green, D. H , and Williams, D. B , *S.A.E Journal*, **54**, 228–37 (1946).
21 Kyropoulos, S , *Refiner Natural Gasoline Mfr.*, **16**, 131–5, 188–92 (1937)
21a. Larsen, R. G , and Bondi, A , *Ind. Eng Chem* , **42**, 2421–7 (1950)
21b Mair, B L , Willingham, C. G , and Streiff, A. J., *J Research Natl Bur Standards*, **21**, 565–607 (1938).
21c. Millett, W. H , *Ind. Eng. Chem* , **42**, 2436–41 (1950)
22. Müller, J , and Neyman-Pilat, E., *J. Inst. Petroleum Tech* , **23**, 669–78 (1947)

23. Murphy, C. M , Romans, J B., and Zisman, W. A., *Trans. Am Soc. Mech. Engrs* , **71**, 561–74 (1949).
23a. Murphy, C. M., and Saunders, C. E., *Petroleum Refiner*, **26**, 479–84 (1947)
23b. Murphy, C M., Saunders, C. E., and Smith, D. C., *Ind. Eng. Chem* , **42**, 2462–8 (1950).
23c. Pritzker, G G., *Petroleum Processing*, **2**, 205–8 (1947).
24. Rochow, E C., "Chemistry of the Silicones", New York, John Wiley and Sons, Inc., 1946
25. Rossini, F D., *Proc. Am. Petroleum Inst.*, **19**, 19th Ann. Meeting, Sec. III, 99–113 (1938), *Oil Gas J.*, **37**, 141–4, 146–7, 149–50, 152–3 (1938); *Refiner Natural Gasoline Mfr* , **17**, 557–67 (1938).
26. Russ, J. M , *Lubrication Eng.*, **2**, 151–61 (1946).
27. Russ, J. M., A.S.T.M. Special Technical Publication No 77, Symposium on Synthetic Lubricants, 1947.
28. Struve, W. S , Benning, A F., Downing, F. B , Lulek, R. N., and Wirth, W. V., *Ind. Eng. Chem* , **39**, 352–4 (1947).
29. Suida, H., and Hawa, J., *Chem. Abstracts*, **41**, 6039 (1947).
30. Sullivan, F. W., Voorhees, V., Neeley, A W., and Shankland, R. V., *Ind. Eng Chem.*, **23**, 604–11 (1931).
31. ter Meulen, H , *J. Inst. Petroleum*, **29**, 237–52 (1943)
32 Thepenier, P., *Ind. papetière*, **20**, 83, 85 (1941); *Chem. Abstracts*, **38**, 4416 (1944).
33. "The Petroleum Data Book", pp. F46–54, Dallas, Petroleum Engineering Publishing Co., 1947.
34. Tomasi, L , *Ann. combustibles liquides*, **13**, 519–45 (1938); *Chem. Abstracts*, **33**, 2693 (1939).
35. Vlugter, J. C., Waterman, H I , and van Westen, H. A , *J. Inst. Petroleum Tech.*, **21**, 661–76 (1935).
36. von Fuchs, G H., and Anderson, A. P , *Ind. Eng. Chem.*, **29**, 319–25 (1937)
37. Weil, B. H , *Nat. Petroleum News*, **37**, No. 27, R512–22 (1945).
38. Wiggins, W R , and Hall, F C , *J Inst Petroleum Tech.*, **22**, 78–98 (1936).

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